Properties and potential use of *Irvingia gabonensis* and *Irvingia wombolu* kernel extract as an eco-friendly wood adhesive

by

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Declaration

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Summary

The wood composite industry relies mostly on formaldehyde-based adhesives derived from non-renewable petrochemical sources. However, due to formaldehyde emission from the composite products bonded with these adhesives and its carcinogenicity, there is a growing need for green alternatives from renewable sources. There is again interest in the domestication of the *Irvingia* tree species due to the potential use of various parts of the tree as raw materials for a wide range of applications such as biodiesel production, cosmetics, perfumes, soap and weight-loss supplements. The aim of this study was to extensively investigate the properties and potential use of *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW) kernel extracts as natural wood adhesives with desirable bonding properties. Bondtite®, a commercial formaldehyde-based adhesive was used as control in this study.

Irvingia gum was extracted from the kernels of IG and IW through three extraction methods. The methods were based on the solvent/solute media and were compared in terms of yield and extract properties. The extracts were characterised using Fourier Transform Infrared (FTIR) spectroscopy to examine functional groups that are present in the extract. Thermogravimetric Analysis (TGA) was used to investigate the thermal stability and decomposition parameters of the extracts. Differential Scanning Calorimetry (DSC) analysis was used to determine melting parameters of the extracts. The strength properties of the extracts were tested using a standard method based on the use of glass fibre paper strips. The FTIR spectra of the *Irvingia* extracts indicate that absorption peak areas of the hydroxyl group decreased with the increase in carbohydrate content. The TGA results showed that the initial decomposition temperature of all extracts, ranges from 138.3–149.11 °C and 129.5–145.3 °C for IG and IW respectively. The curing temperature could therefore be set around 150 °C. It was discovered through DSC analysis that *Irvingia* adhesives have a lower melting temperature compared with other wood adhesives. The strength properties results showed that tensile strength per gram of the kernel extracts ranged from 5.0 to 13.6 KN/mg and 7.4 to 14.7 KN/mg for IG and IW, respectively. The moduli of elasticity ranged from 17.9 to 44.1 GPa and 31.3 to 46.7 GPa for IG and IW, respectively.

To enhance the strength properties of the extracts, further investigation was carried out on the effect of four different modifiers on *Irvingia* kernel extracts earmarked for use as natural wood adhesives. Hexamethometylmelamine (Hexamine) was used as a crosslinker to develop an effective crosslinking reaction between methoxyl groups in hexamine and hydroxyl groups in the

extracts, modifiers and wood. FTIR, DSC and TGA were conducted for advanced characterisation of the modified adhesives properties. The adhesive properties of the modified extracts were tested on wood veneers according to the American Society for Testing and Materials standard (ASTM D – 906-98). The successful modification of the *Irvingia*-based wood adhesives was proven with the emergence of new peaks in the FTIR results. The derivative thermogravimetric results showed that $(DTG)_{MAX}$ temperature for all modified samples was between 460 °C and 480 °C, except for the glyoxal-modified samples (IWLY and IGLY). The DSC results showed that the curing temperatures of all *Irvingia* adhesives are in a close range, irrespective of species and modification methods between 112 and 114 °C. The shear strength of the modified adhesives ranged from 1.72 to 4.05 MPa and 1.74 to 3.89 MPa for IG and IW respectively. The highest values of adhesive shear strength of the modified samples were about 16% higher than panels bonded with IGN (unmodified) adhesives. In a nutshell, modification of the *Irvingia*-based adhesives resulted in better properties, which contributed to the strength of the adhesives as observed in this study. The main advantage of these modified adhesives is that they do not contain formaldehyde or phenol, both of which are considered potent environmental contaminants.

Finally, the possibility of using the natural-based adhesive derived from *Irvingia* kernel extracts on wood panel products was examined. The modulus of elasticity (MOE) of the panels ranged from 458 to 1281 MPa and 660 to 1 580 MPa for IG and IW while the modulus of rupture (MOR) of the panels ranged from 3.31 to 7.38 MPa and 5.11 to 6.88 MPa for IG and IW respectively. The mean values of MOR and MOE for the panels produced with *Irvingia*-based adhesives were 5.8 and 1251 MPa respectively. The values are within the minimum required MOR and MOE (5.5 and 1034 MPa respectively) for panel grade 1-L-1 as specified in the American National Standard (ANSI) A208.1. These panels are recommended to be used as core material for solid doors.

Opsomming

Die saamgestelde-hout-produkte industrie maak hoofsaaklik gebruik van formaldehied-gebaseerde lyme wat verkry word van nie-hernubare petrochemiese bronne. As gevolg van die formaldehied vrylatings van die saamgestelde produkte wat verbind word met die lyme asook die carcinogeniteit, is daar 'n toenemende behoefte aan groen alternatiewe van hernubare bronne. Daar is tans 'n toenemende belangstelling in die kweek van *Irvingia* boom spesies as gevolg van die potensiaal in die gebruik van die rou materiaal in verskeie aanwendings. Die gebruikse sluit in bio-diesel produksie, kosmeties, perfuum, seep, gewig verlies aanvullers en dies meer. Die doel van die studie was om die eienskappe en potesiële gebruik van *Irvingia gabonensis* (IG) en *Irvingia wombolu* (IW) pit ekstraksie as natuurlike hout lym, met aanvaarbare las eienskappe, volledig te ondersoek. Bondtite®, 'n kommersiële formaldehied-gebaseerde lym was gebruik as kontrole in die studie.

Irvingia gom was onttrek van die pitte van IG en IW deur drie onttrekkings metodes. Die metodes was gebaseer op die oplossing/opgeloste middel en vergelyk in terme van opbrengs en aftreksel eienskappe. Die ekstraksie was geklassifiseerd volgens die Fourier Transvorm Infrarooi (FTIR) spektroskopie om die funksionele groepe wat teenwoordig is te eksamineer. Termogravimetriese Analise (TGA) was gebruik om termiese stabiliteit en ontbindingsparameters te ondersoek. Differensiële Skandering Kalorimetrie (DSK) analise was gebruik om die smeltpunt van die ekstrasies te bepaal. Die sterkte eienskappe van die ekstraksies is bepaal deur die standaard metode van glasvesel-papier repe. Die FTIR spektra van die *Irvingia* ekstrasies toon die absorbsie piek areas van die hidroksielgroep verminder in koolhidraat inhoud. Die TGA resultate toon dat die aanvanklike ontbindings temperatuur van al die ekstraksies, wissel tussen 138.3–149.11 °C en 129.5–145.3 °C vir IG en IW onderskeidelik, dus, kan 'n settings temperatuur van 150 °C gebruik word. Dit was ondervind, deur die DSK analise, dat *Irvingia* ekstrasies 'n laer smeltpunt het as ander hout lyme. Die sterkte eienskappe resultate toon dat trekkrag per gram van die pit ekstraksies wissel tussen 5.0 tot 13.6 KN/mg en 7.4 tot 14.7 KN/mg vir IG en IW, onderskeidelik. Die modulus van elastisiteit wissel van 17.9 tot 44.1 GPa en 31.3 tot 46.7 GPa vir IG en IW, onderskeidelik.

Verdere ondersoek is ingestel om die sterkte eienskappe van die *Irvingia* ekstraksies te verbeter deur middel van vier natuurlike aanvullers vir hout lym te gebruik. Hexamethometylmelamien (Hexamien) was gebruik as kruisverbinding om 'n effektiewe kruisbinding reaksie te vorm

tussen die metoksielgroepe in hexamien en die hidroksielgroepe in die ekstraksies, asook tussen die aanvullers en die hout. FTIR, DSK en TGA was gebruik vir die gevorderde karakterisering van die gemodifiseerde lym eienskappe. Die lym eienskappe van die gemodifiseerde ekstraksies was getoets op hout spaanders volgens die Amerikaanse Gemeenskap vir Toets en Materiaal standaarde (ASTM D – 906-98). Die verbeterde gewysigde *Irvingia* hout gebaseerde lym was bewys deur die verskyning van nuwe FTIR piek resultate. Die afgeleide termogravimetriese resultate toon dat die $(DTG)_{MAKS}$ temperatuur vir al die gemodifiseerde monsters tussen 460 en 480 ºC wissel, behalwe vir die glyoksal gemodifiseerde monsters (IWLY en IGLY). Die DSK resultate toon dat die set temperatuur (112 – 114 ºC) van al die *Irvingia* ekstrasies naby mekaar is, ten spyte van spesie en modifiserings metode. Die skuifkrag van die gemodifiseerde lyme wissel van 1.72 tot 4.05MPa en 1.74 tot 3.89MPa vir IG en IW onderskeidelik. Die laagste skuifkrag waarde vir die *Irvingia* lyme was hoër as die die 1MPa vir bord produkte van kruis laag verbinding lae, volgens die EN 16352 (2015) standaard. In kort, die modifisering van die *Irvingia* gebaseerde lyme, het beter resultate tot gevolg gehad wat bydra tot die sterkte van die lym in die studie. Die hoof voordele van die lyme is dat hulle nie formaldehied of fenol, beide is skadelik vir die omgewing, bevat nie.

Laastens, die moontlikheid van die gebruik van natuurlike lyme vanaf *Irvingia* pit ekstraksies op hout bord produkte, was ondersoek. Die modulus van elastisitet (MOE) van die panele wissel van 458 tot 1281MPa en 660 tot 1580MPa vir IG en IW, terwyl die breekkrag (MOR) van die panele wissel van 3.31 tot 7.38MPa en 5.11 tot 6.88MPa vir IG en IW onderskeidelik. Die gemiddelde waardes vir MOR en MOE vir die *Irvingia* gebaseerde lym vervaardigde panele, was 5.8 en 1251MPa onderskeidelik. Die waardes is binne die minimum vereistes vir MOR en MOE (5.5 en 1034MPa onderskeidelik) vir paneel graad 1-L-1 soos gespesifiseerd in die ANSI A208.1. Die panele word aanbeveel vir die gebruik as kern-materiaal in soliede deure.

Dedication

This dissertation is dedicated to

The glory of God,

And to the blessed memory of my father, Mr Ezekiel Oke Alawode
without whom none of my success would have been possible

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List of publications

This dissertation is based on the following publications, which in the text are referred to by their titles and are presented within the results and discussion chapters of this dissertation.

Journal articles

1. Publication I

Properties and characteristics of novel formaldehyde free wood adhesives prepared from *Irvingia gabonensis* and *Irvingia wombolu* seed kernel extracts

Alawode A.O, Amiandamhen S.O, Meincken M, Tyhoda L

International Journal of Adhesives and Adhesion (*under review*)

2. Publication II

Evaluation of *Irvingia* Kernels extract as biobased wood adhesive

Alawode A.O, Amiandamhen S.O, Meincken M, Tyhoda L

Journal of Adhesion Science and Technology (*under review*)

3. Publication III

Performance evaluation of a natural based adhesive derived from *Irvingia* wood species kernel extracts on wood panel production

Alawode A.O, Amiandamhen S.O, Meincken M, Tyhoda L

Composites Part B: Engineering (*under review*)

4. Publication IV

Techno-economic analysis for small-scale production of *Irvingia* based adhesive in South Africa

Alawode A.O, Amiandamhen S.O, Meincken M, Tyhoda L (*in preparation*)

List of conference contributions

Presentation I

Alawode AO, Amiandamhen SO, Meincken M, Tyhoda L (2018) Properties and Potential Use of *Irvingia gabonensis* and *Irvingia wombolu* Kernel extracts as a Natural Wood Adhesives. IRG49 Scientific Conference, April 29-May 2, 2018, Sandton Hilton Hotel, Sandton, Johannesburg, South Africa.

Presentation II

Alawode AO, Amiandamhen SO, Meincken M, Tyhoda L (2018) Natural Wood Adhesives Prepared from *Irvingia gabonensis* and *Irvingia wombolu* Kernel extracts to reduce formaldehyde emissions. Forest Products Society 72nd International Convention, June 12–14, 2018, Monona Terrace Community and Convection Centre, Madison, Wisconsin, USA.

Presentation III

Alawode AO, Amiandamhen SO, Meincken M, Tyhoda L (2018) Performance evaluation of a natural based adhesive derived from *Irvingia* kernel extracts on wood panel production. Third International Conference on Composites, Biocomposites and Nanocomposites, November 7–9, 2018, Nelson Mandela Bay Stadium, Port Elizabeth, South Africa.

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Chapter 1

General introduction

1.1 Background and motivation

Wood adhesives play a vital role in the production of various wood composites and the increase in the production of reconstituted wood panels has resulted in an increase in the consumption of adhesives which are typically formaldehyde and petroleum-based (Carvalho et al. 2014). Formaldehyde-based adhesives such as urea formaldehyde (UF), phenol formaldehyde (PF) and melamine-urea-formaldehyde (MUF) are those most commonly used in the wood processing industries because of their superior adhesion properties (Khosravi et al. 2010; Zhang et al. 2014). They exhibit several advantages such as good adhesion to different lignocellulosic substrates, high water resistance (except UF), low initial viscosity, resistance to environmental degradation, and excellent thermal stability (Carvalho et al. 2014; Dongre et al. 2015; Sulaiman et al. 2013). However, despite these advantages, they have one major limitation, which is the emission of formaldehyde. This has been categorised to be carcinogenic by the Environmental Protection Agency (EPA) since 2008 (Langenberg et al. 2010). Therefore, there is a need for the development of wood adhesives from renewable sources that will be formaldehyde-free and possess comparable strength properties to commonly used synthetic adhesives.

Renewable material-based adhesives are made from plant or animal sources and have various advantages over synthetic adhesives. They are developed from materials which are abundant, sustainable, environmentally friendly and low cost. However, they have some shortcomings such as low gluing strength and low biodegradation resistance. Renewable materials have been used to develop wood adhesives for the production of wood composite products such as plywood, particleboard, and oriented strand board. Several efforts have been made by various researchers using different biological materials such as lignin, tannin, furfural, or soybean either to reduce the formaldehyde content in adhesives or to even develop adhesives completely from natural materials (Alonso et al. 2005; Jang et al. 2011; Zhang et al. 2014). Khosravi et al. (2010) investigated the possibilities of using soy protein isolate (SPI) and wheat gluten (WG) as a binder for particleboards. The results showed that both SPI and WG could be used as binders for particleboards. Moubarik et al. (2009) developed natural-based adhesives from cornstarch and tannins to produce particleboard. The authors discovered that particleboard bonded with formaldehyde-free cornstarch-tannin adhesive showed comparable mechanical properties to the

panels made with the commercial UF resin. Wang et al (2012) developed a starch-based wood adhesive using grafting modification treatment with vinyl acetate monomer onto waxy cornstarch. It was concluded that it is possible to synthesise a starch-based wood adhesive with good adhesion that can be used at room temperature.

There has been limited research on the utilisation of wood adhesives based on natural seed gums. Norström et al. (2014) evaluated the possibilities of utilising natural gums from the seed of locust bean, guar, xanthan, and tamarind as wood adhesives. The authors reported high molar mass and viscosity for the gums, with locust bean gum giving the best bonding performance. This study seeks to investigate the potentials of the extracts from kernels of *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW) species as raw material for the development of environmentally friendly wood adhesives. The *Irvingia* species are underutilised, highly valued fruit trees, native to Africa and Southeast Asia and belong to the family *Irvingiaceae*. *Irvingia* was described as a genus in 1860 (Ainge and Brown 1998). The species include *Irvingia smithii*, *Irvingia malayana*, *Irvingia gabonensis* (IG), *Irvingia wombolu* (IW), *Irvingia grandiflora*, *Irvingia robur,* and *Irvingia malayana* in Southeast Asia (Singh 2007). In Africa, two species are common: IG and IW. These are forest fruit trees found widely in Western and Central Africa. *Irvingia* species are commonly known as the African mango, Dika nut, bush mango or wild mango (Ikechukwu and Salome 2013). Etebu and Tungbulu (Etebu and Tungbulu 2016) made a distinction between the two species, noting that IG has a sweet edible pulp while IW has a bitter inedible pulp.

In Africa and Asia, potential industrial applications of *Irvingia* kernels have been reported by various researchers including cooking oil, margarine, perfume, soap and pharmaceutical binders. (Ainge and Brown 1998). The possibility of using its oil extract as a possible alternative fuel for use in diesel engines was also investigated (Bello et al. 2011). Attempts have been made by some researchers to use *Irvingia* kernels extracts as a binder in pharmaceutical applications (Eraga et al. 2014; Ikechukwu and Salome 2013; Uzondu and Okor 2013). Ikechukwu and Salome (2013) investigated the physicochemical characterisation of IW gum in tramadol-encapsulated granules. It was discovered that IW gum contains alkaloids, flavonoids, saponin, tannins and glycosides. They concluded that natural gum from IW has good potential to be used in formulating normal tramadol capsules. In a similar study, Eraga, (2014) inferred from the results of their investigation that the suspension prepared with the co-precipitate of IG gum and gelatin as suspending agent appears to be superior to those prepared with the gum or gelatin alone.

Ikhatua et al. (2010) reported that fungus (*Aspergillus fumigatus*) is the predominant isolate and the pathogen of spoilage of *Irvingia* seeds. Awono (2002) and Ewane (2010) reported that the proximate analysis of the nutritive composition of healthy kernels of IG and IW obtained from

retailers showed no significant differences in some nutritive components. The authors concluded that there was no significant difference in the proximate analysis between healthy and spoilt kernels. In a related study, Ikhatua and Falodun (2012) reported that there were no significant differences in the chemical composition of both healthy and spoilt kernels of the *Irvingia* species. Because of this, rejected seeds may be utilised for the gum formulation. This is another way of waste utilisation since the chemical composition remains unaltered irrespective of their physical appearance. *Irvingia* kernel extracts are biomaterials with the potential to be used as renewable adhesives and serve as a green and cost-effective wood adhesive with desirable bonding properties. Extracts of *Irvingia* species are byproducts obtained after the kernel fat content has been used for the manufacture of various products such as cosmetics, biofuel, cooking oil, season cubes, soaps and confectionaries (Bello et al. 2011; Ekpe et al. 2015). To the best of my knowledge, this is the first study evaluating the use of extracts from these species as wood adhesives. This study describes the feasibility of extracting and formulating adhesives from *Irvingia* kernels for wood composite applications.

1.2 Research aim

The general aim of this study was to develop an alternative wood adhesive from raw materials derived from renewable resources. The study utilized extracts from kernels of *Irvingia gabonensis* and *Irvingia wombolu* species as an environmentally friendly wood binder. Early studies showed that formaldehyde-based adhesives are the most commonly used in the wood processing industries because of their superb adhesion properties. However, the adverse effect of formaldehyde emission on human health and environment had been well documented and cannot be overemphasised. Hence, there is a need for alternatives to the formaldehyde-based wood adhesives. Many kinds of research are presently being carried out to find more environmentally friendly wood adhesives. The *Irvingia* species is an underutilised highly valued Africa indigenous tree that can play an important role in the development of eco-friendly wood adhesives. Prospects also abound for binder development from this species since some studies report numerous potential uses. Presently, research findings showed that extracts from its kernels have not been fully utilised for industrial applications. As with other natural adhesives, property improvement is usually toward changing the molecular structure by modifying them with various hardeners and crosslinkers and it is well documented that modification improves its adhesive properties. As a result, this work examined the properties and potential use of the kernel extracts from *Irvingia* species trees for making environmentally friendly wood binders either as a partial or full replacements for synthetic binders.

1.3 Objectives of the study

The following objectives were identified and addressed to accomplish the general aim of the study:

Objective 1: To characterise the chemical composition of *Irvingia gabonensis* and *Irvingia wombolu* kernels; to extract adhesives from the kernels using three methods and evaluate their physicochemical properties.

To address this objective, proximate analysis of the kernels of both species was carried out to establish the percentage composition of carbohydrate, protein, fat, ash and moisture content using the Association of Official Analytical Chemists Methods (AOAC Methods. 2005). Three different methods, which include water, sodium chloride, and metabisulphite were compared for the extraction of the binder from the kernels (Eraga et al. 2014; Ikechukwu and Salome 2013; Ogaji et al. 2012). Advanced characterisation of the formulated binder was carried out using thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopic (FTIR) and differential scanning calorimetry (DSC) analysis. The physical and mechanical properties of the adhesives formulated were also evaluated and the results are presented in Chapter 4 of this dissertation.

Objective 2: To modify the formulated binders using different materials and evaluate their physicochemical and mechanical properties

The results from objective 1 formed the basis for objective 2 – modification of the extracts to enhance the adhesivity. The water extraction method was chosen to start with because it produced *Irvingia* extract with the best performance on the basis of objective 1. This objective was addressed by selecting different hardeners which include; glyoxal, epichlorohydrin, and glutaraldehyde for the modification process. Hexamine was used as the crosslinker. Acid/base modification processes were also investigated using hydrochloric acid and sodium hydroxide. Advanced characterisation of the modified binder was also carried out using thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopic (FTIR) and differential scanning calorimetry (DSC) analysis. The physical and mechanical properties of the adhesives modified were also evaluated and the results are presented in Chapter 5 of this dissertation.

Objective 3: To produce wood composites from the adhesives developed and evaluate the physical, chemical and mechanical properties of the board produced.

Following up on objective 2, particleboards were produced using *Irvingia* based adhesives developed from different hardeners, namely epichlorohydrin, glutaraldehyde and glyoxal with

hexamine as a crosslinker in order to establish the adhesive that gives best board mechanical properties and dimensional stability. This objective was addressed by using pine (*Pinus elliottii*) wood particles, for the production of the particleboard. The physical and mechanical properties of the composite panels were evaluated, and the results are presented in Chapter 6 of this dissertation.

Chapter 2

Literature review: Production of formaldehyde-free wood adhesive from renewable resources

2.1 Introduction

An adhesive is any substance capable of binding materials together through surface attachment (Okemini and Dilim, 2015). Adams (2005) also describes an adhesive as any substance that joins surfaces together and resists their separation. The use of adhesives for bonding materials has long been in existence with natural gums, plant resins and animal glues made from rendered animal products being considered as the first adhesives. Egg whites were later used as an adhesive to decorate parchments with gold leaf in the Middle Ages in Europe and as modernisation continued, new patents were issued by using rubber, bones, starch, fish, and casein (Liu and Li, 2002). Industrialisation of adhesive production started in Holland around 1690 and it was later introduced to England around 1700 (Adams 2005).

Prior to the emergence of petroleum-based adhesives, the use of renewable material-based adhesives had been in place. These were extensively used prior to the advent of synthetic adhesives but were set aside because of their low bonding strength and hydrophilicity. Renewable materials-based adhesives come from various sources including; animal, casein vegetable protein, starch, blood albumin, sodium silicate, mucilage, pastes, rubber, types of cement, asphalts, gums and shellacs. Renewable material-based adhesives offer several advantages over synthetic adhesives. Although renewable material-based adhesives have numerous benefits over synthetic adhesives, they still have certain disadvantages such as low strength, susceptibility to microbial attack, limitation to dry interior applications and restrictions to the joining of low-strength materials.

Chemical modification of renewable material-based adhesives has been suggested as a possible means of producing strong and durable adhesives without compromising environmental sustainability (Alonso et al., 2005; Liu and Li, 2002, 2004). Renewable material-based adhesives such as those based on protein, starch, casein, furans, enzyme, lignin, tannin from wattle and acacia (Chen et al. 2012; Dongre et al. 2015; Khosravi et al. 2010; Santoni 2013) have been the subject of extensive research in the recent past. Technologies involved in the production of these adhesives seem to raise the production cost above that of formaldehyde-based adhesives and their commercial production remains pending (Langenberg et al., 2010). According to Langenberg et al., (2010) all technologies currently considered

'green' or natural consist of a large portion of petrochemically derived components or renewable materials chemically modified with petrochemicals.

The industrial application of adhesives is not limited only to bonded wood products but also extends to paper products, paints, and finishes. In fact, the production of building materials such as plywood and other laminated veneer products, particleboard, oriented strandboard, fibreboard, laminated beams and timbers, edge-and-jointed products, windows and frames, architectural doors, and fiberglass insulation involves huge amounts of adhesives to assemble them in residential and industrial construction, particularly in panelised floor and wall systems. In addition, substantial amounts of adhesives are used in non-structural applications such as furniture, overlays, floor coverings, countertops, ceilings, wall tiles, as well as trims and accessories. Johnson (2000) reports that over USD7.4 billion were spent on wood adhesives in 1999 by the forest products industries in the United States and Canada.

In a nutshell, wood adhesives play a major role in the production of wood composites as they are used extensively in the wood industry for different purposes which include assembly work, manufacture of paper and papyrus, wood composite production, bonding and veneering of wood (Adams 2005).

2.2 Classification of adhesives

There are various classifications for wood adhesives by different authors, but the broadest classification scheme is to categorise an adhesive as being manufactured from materials that are either naturally occurring or synthetic. The classification of adhesives into synthetic and naturally occurring categories is usually far too broad for many practical purposes. Adhesives have been classified based on several common methods that satisfy most purposes such as function, chemical composition, mode of application or reaction, physical form, cost, and end-use. They can also be classified on three principles which include the origin of the primary components, curing temperature and durability (Muthike and Githiomi, 2011). On the basis of curing method, they can further be classified into reactive and non-reactive adhesives. Reactive adhesives include UV light-adhesives, heat-reactive adhesives, and moisture-curing adhesives. Non-reactive adhesives are mainly drying, hot melt and pressure sensitive adhesives. Adhesives can be further classified on basis of load-carrying capacity which may be structural, semi-structural and non-structural adhesives (Kottakota, 2015). Furthermore, they can be categorised as thermoplastic and thermosetting adhesives (Kwon et al., 2014). These classifications and distinctions overlap to some degree. Adhesives produced from natural materials such as dextrin, starch, protein or natural rubber; and those developed from synthetic polymers such as polyvinyl acetate, polyvinyl alcohol, polyesters, acrylics, neoprene, butyl rubber, and phenolic are described as low-to medium-performance products. Adhesives produced from polymers such as epoxy, polysulfide, polyurethane, cyanoacrylate, and silicone

are termed as high-performance products because of their enhanced properties such as bond strength, elongation capacity, durability or environmental resistance (Kottakota, 2015).

2.2.1 Synthetic wood adhesives

Synthetic adhesives are largely made up of chemicals not specifically extracted from plant and animal products. According to Eckelman (1997), "… synthetic resins are man-made polymers which resemble natural resins in physical characteristics but which can be tailored to meet specific woodworking requirements". The development of adhesives from synthetic sources has caused a steady replacement of bio-based products which were in use until the 1920s. Judge (1921) lists the adhesives available before the advent of synthetic adhesives for aircraft and automobile manufacture as the following; animal glues (hide, bone or hoof), fish glue, liquid glues (animal glues in liquid, ready-to-use state), marine glue (made from India rubber, naphtha and shellac), casein glues, waterproof glues (modified 'ordinary glue'), vegetable glues, flexible glue (modified animal glue), and albumen glues.

Synthetic adhesives include phenol formaldehyde, urea formaldehyde and melamine formaldehyde. They are produced from industrial raw materials that have fossil origins such as urea, phenols, formaldehyde, melamine, furan, epoxy, cellulose esters, ethers, alkyd, acryl esters, polyamide, polystyrene, and polyvinyl alcohols (Muthike and Githiomi, 2011). Formaldehyde-based resins are one of the possible sources of formaldehyde emission and this has been a subject of concern in the formaldehyde resin-bonded wood-base panel industry for a number of years (Kim & Kim, 2004; Nikvash et al., 2013; Dongre *et al.*, 2015; Elbadawi et al., 2015). There have been a series of reports emphasising the consideration of formaldehyde emission given by the United States Environmental Protection Agency on its adverse effect on both the environment and end users. In addition, formaldehyde-based wood adhesives are mainly produced from raw materials derived from crude oil and their prices depend largely on the current oil price (Langenberg et al., 2010; Dongre *et al.*, 2015). Furthermore, there are reports that crude oil resources are depleting gradually. This has increased concerns and the need for substituting synthetic adhesives with alternatives from renewable sources which are capable of giving the desired performance, not harmful to the environment, available for market supply and cost-effective (Langenberg et al., 2010). Table 1 summarises various synthetic resins and their attributes.

Table 1: An overview of various synthetic resins and basic attributes

Type	Form	Characteristics	Application	Products
THERMOSETTING				
UF (Urea formaldehyde)	Powder or liquid blended with melamine and other resins	High in wet and dry strength. Moderately durable under damp conditions	Applied at room temp and cured or some are hot pressed at high temperatures.	Plywood and particleboard
MF (melamine formaldehyde)	Powder with or without catalyst	High in wet and dry strength. Very high resistance under damp conditions.	Mix with water at room temperature and cure at high temperature.	Hardwood plywood, end jointing, edge laminating
PF (Phenol formaldehyde)	Aqueous alkaline dispersion for plywood and powder or liquid for OSB flakeboard	High in wet and dry strength. Very high resistance in damp conditions. More resistance than the wood to high temp and chemicals.	Film form or powder and liquid at room temp. Most require hot pressing.	Main adhesive for exterior softwood, plywood and flakeboard
Resorcinol and Phenol-resorcinol formaldehyde	Liquid with separate hardeners. Most expensive of the formaldehyde-based adhesives	High in wet and dry strength. Very high resistance under damp conditions. More resistance than the wood to high temp and chemicals.	Mix with hardener and apply and cure at room temperature.	Laminated timber and joints that must withstand severe conditions e.g. I joist and glulam
Isocyanates	Liquid resins or water emulsions	Excellent adhesion to wood and high chemical and temp resistance.	Very rapid cure on application of heat or in presence of moisture	Limited use in structural flakeboard, jointing. High cost.
THERMOPLASTIC				
PVA thermoplastic	Liquids	High dry strength, low resistance to temp and moisture.	Liquid ready to use, room cure.	Furniture, flush doors, plastic laminates.
Hot melt adhesives (Polyamides, polyurethane (PU), polyolefins etc.	Solid	Gap filling, moisture resistance, lower strength.	Melting or spread	Furniture, plastic overlays, patching, panel edging.

Source: Jones (2007)

2.2.1.1 Effects of formaldehyde emissions

Volatile organic compounds, sometimes referred to as VOCs, are organic compounds that easily become vapours or gases. They contain elements such as carbon, chlorine, oxygen, fluorine, bromine, sulphur or nitrogen. Formaldehyde is one of the volatile organic compounds and is considered to be gaseous at room temperature, but it can polymerise forming para-formaldehyde, and it readily dissolves in water forming methylene (Moubarik *et al.*, 2010). It is considered a threat to the environment and to humans. Emissions of formaldehyde vapour from many consumer products produced with formaldehyde-based adhesives cause consumer dissatisfaction and health-related complaints (Kim and Kim, 2004). These emissions from formaldehyde have been reported to cause diverse sicknesses which depend on the duration of exposure. Long-term exposure to volatile organic compounds can cause damage to the liver, kidneys, and central nervous system. Short-term exposure to volatile organic compounds can cause eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment (Sumin Kim 2009). In fact, according to a report published by the International Agency for Research on Cancer (IARC), formaldehyde has been reclassified as a Category 1-known human carcinogen (Langenberg et al., 2010). Many authors have developed and used different methods to measure the levels of formaldehyde emissions. These methods include the Fraunhofer WKI method, perforator method, and the desiccator method (Kim and Kim, 2004; Lum et al., 2014; Song *et al.*, 2015). Kim successfully used gas chromatography to determine formaldehyde emissions and he concluded that the results obtained were similar to those obtained using the perforator method which is the most commonly used method (Kim and Kim, 2004).

2.2.1.2 Phenol partial replacement in formaldehyde-based adhesives

There is a series of reports from literature whose focus is on the reduction of formaldehyde emission. Various researchers incorporated different materials such as tannin, lignin and cashew nut shell liquid (CNSL) as a replacement for UF, MUF and PF adhesives (Kim 2009, 2010; Langenberg et al., 2010). For instance, a modified wheat protein was incorporated with UF to reduce formaldehyde emission from urea formaldehyde, but the panels produced exhibited poor physical properties, particularly in water absorption and thickness swelling (Nikvash 2012; Nikvash et al., 2013). Incorporation of lignin as a substitute in PF resin has also been reported by various authors and it appears to be the predominant application for lignin used in adhesives (Alonso *et al.*, 2005; Khan and Ashraf, 2006; Wang *et al.*, 2006; Donmez et al., 2008). The attractiveness of lignin as a phenol replacement in wood adhesives is as a result of its phenolic nature and reactivity with formaldehyde (Langenberg et al., 2010). Çetin and Özmen, (2003) investigated the extent to which organosolv lignin, using methylolation modification, could replace phenol in PF resins designed for application as an adhesive to bond

particleboards. The authors reported that tensile testing of resin-impregnated strips showed that the properties of modified lignin resins were at least good as those of PF resin and concluded that renewable resources such as lignin have potential as a substitute for phenol in PF resin systems. Steam explosion lignin was also used to partially replace phenol through ternary gradual copolymerisation and it was discovered that phenolate modification improved the reactivity of lignin by increasing its phenolic content and decreasing its methoxyl content. The authors concluded that the properties of the adhesive produced met the required standard when the steam explosion lignin replacement percentage of phenol was within the range of 10–70 wt% (Zhao et al. 2016). Atta-Obeng (2011), in his study of reinforced phenol formaldehyde with microcrystalline cellulose (MCC) at different loading rates (0–10%), used lap shear tests to evaluate the strength of the cellulose-reinforced adhesive system and reported that the cellulose reinforcement lowers the curing temperature, thermal stability as well as increasing the shear strength with the addition of cellulose. Most reports in the literature describe partial phenol substitution of lignin into PF resins while only very few authors describe the total replacement of the PF resin component.

Tannin incorporation into adhesive formulations has been widely reported over the last few decades in many articles to reduce formaldehyde emission in an adhesive system (Pizzi 2000; Sellers 2001; Langenberg et al., 2010). The reason is not only for emission reduction but also to reduce cost, increase crosslinking or adhesive reinforcement, promote cure and efforts to improve water resistance. Condensed tannins are polyphenolic materials and are generally comprised of the oligomeric flavonoid-type structures in Figure 1 below. They are the only useful tannin in the development of wood adhesives or resins and the attractiveness of using these tannins in wood adhesives can be derived from similar reactivity and crosslinking chemistry with formaldehyde as that found for phenol-and resorcinol-formaldehyde systems (Langenberg et al., 2010). Figure 1 shows the chemical structure of resorcinolic type condensed tannins with 4–6 interflavanyl linkages present in quebracho extracts (left); and phloroglucinolic type condensed tannins typically present in pine species with 4–8 interflavanyl linkages (right).

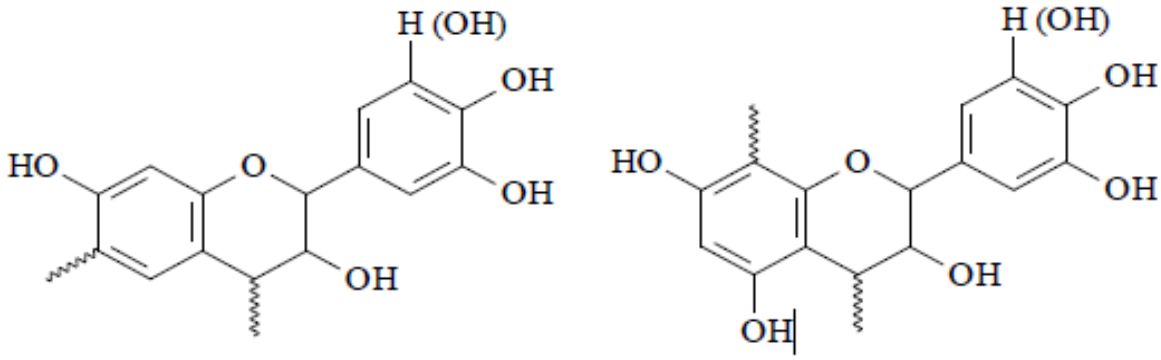


Figure 1: Chemical structure of condensed tannins (Langenberg et al. 2010)

Elbadawi et al. (2015) studied the influence of adding a blend of tannins extracted from the bark of two *Acacia* species and UF on the mechanical and physical properties of laboratory particleboards made from underutilised raw materials. The results obtained revealed an increase in the modulus of rupture (MOR), modulus of elasticity (MOE) and internal bonding (IB) of these panels when a small amount (5%) of blend tanning was added. The authors found that higher percentages (10% & 15%) decrease the mechanical properties. They also discovered that the addition of tannin and UF did not improve the physical properties (thickness swelling and water absorption after 24 h immersion in water), which remained comparable to the control panels. In a related study, natural wattle tannin was used to replace UF in the formaldehyde-based resin system in order to reduce formaldehyde and emission of volatile organic compounds (VOCs) from the adhesives used between plywood and fancy veneers (Sumin Kim 2009). The author added polyvinyl acetate (PVAc) to the natural tannin adhesives to increase the viscosity of the tannin adhesive for surface bonding. Furthermore, he used different standard formaldehyde emission tests such as the desiccator method, field and laboratory emission cell (FLEC) and VOC analyser to determine the formaldehyde and VOC emissions from engineered flooring bonded products. In their investigation, they observed that Total Volatile Organic Compounds (TVOc) emissions were slightly increased as PVAc was added to natural tannin, but all adhesives satisfied the E_1 grade (below 1.5 mg/L) and E_0 grade (below 0.5 mg/L). In relation to the bonding strength of the adhesives produced, the author reported that tannin/PVAc hybrid adhesives were higher than those of the natural tannin adhesive (Sumin Kim 2009). Bertaud *et al.*, (2012) in their quest to reduce formaldehyde emissions from wood panels and to develop green adhesives, used a blend of natural phenolic polymers of tannins and lignin to investigate their possibility as substitutes for petroleum-based chemicals in the production of wood panels. They stated that the tannin/lignin adhesive formulation compounded from 60% commercial mimosa tannins with hexamine and 40% glyoxylated softwood Kraft lignin, gave the best particleboard properties and concluded that this green adhesive based on the lignin/tannin formulation significantly reduced the formaldehyde emission of the particleboards. Similarly, tannin-adhesives were also derived from *Stryphnodendron adstringens* (Mart) Coville and combined with commercial phenol-formaldehyde (PF) adhesive in order to reduce formaldehyde emission from the plywood panel produced (Carvalho et al. 2014).

2.2.2 Renewable-based wood adhesives

Renewable adhesives are developed from naturally occurring materials such as animal or agricultural byproducts. They are sometimes referred to as renewable, green adhesives, natural adhesives, bio-derived adhesives, bioresins, and bio-adhesives (Jones, 2007; Papadopoulou, 2009; Moubarik *et al.*, 2010; Langenberg, 2010). According to Jones (2007), bio-derived adhesives can be defined as "… materials of natural, non-mineral or non-petroleum-based

origin that can be used either in their natural state or after a small modification. They are capable of reproducing the behaviour and performance of synthetic resins". The use of renewable adhesives was dominant until 1940 when there was a gradual decline. Up to World War II, the dominant adhesives for bonding wood were made from renewable sources (Lambuth 1989). Renewable adhesives lost much of their significance on the emergence of synthetic adhesives with specific properties; constant quality and lower cost (Papadopoulou, 2009). More recently, the use of renewable adhesives for the manufacture and production of reconstituted and engineered wood products has been gaining increasing attention owing to a number of drivers. The most important of these drivers relates to government legislative changes to minimise the health effects relating to product emissions of volatile organic chemicals (VOCs), most notably formaldehyde, and the use of renewable materials as a cost-effective replacement for petrochemical components of adhesives (Langenberg et al., 2010). Nikvash, et al., (2013) also report that there has been renewed interest in the utilisation of natural adhesives instead of synthetic resin for bonding wood composites. Research findings have indicated that all renewable adhesives when formulated and modified correctly can make a joint that will be stronger than the wood itself and in choosing adhesives for wood composite production, cost and ease of application are the main factors (Keimel 1994). Renewable adhesives are made from plant or animal sources such as starch, soybean, animal waste, casein from milk and byproducts of the meat processing and tannin industries. The advantages of renewable adhesives over synthetic adhesives include ready availability, no emission of formaldehyde or any hazardous substance which can affect human health, made from renewable natural resources and cost-competitive to formaldehyde-based adhesives. They are developed with a relatively low level of processing because they are made up of naturally occurring materials.

According to Emeje and Isimi (2008), adhesives from plants are mainly long chain, straight or branched chain polysaccharides that contain hydroxyl groups which bond to water molecules and are generally non-toxic and widely available. Momoh et al., (2011) also report that natural gums are widely available with specific properties, which offer the flexibility of applications. It was observed that in North America there are plans currently underway to change from petrochemical adhesives to those incorporating natural and renewable materials. Also, it was reported that there is a reasonable expectation to see changes within the next 5 to 10 years in Australia and New Zealand, especially as the consumer becomes more environmentally aware (Langenberg et al., 2010).

The categorisation of renewable adhesives is based on their origin: plant, animal, enzyme-based or carilite adhesives. Carilite is not necessarily a natural product though it is made from renewable resources; it is an alternative binder that does not release formaldehyde (Langenberg et al., 2010). There are different sources of renewable materials for natural

adhesives and these include tannins, lignin, oils, proteins (in particular soy protein) and other sources as described in Figure 2.

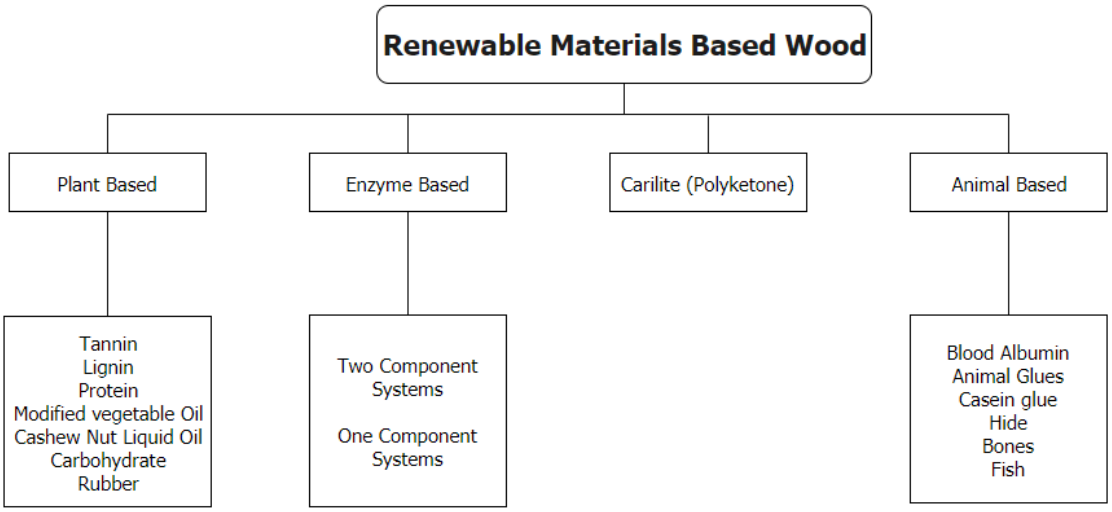


Figure 2: Classification of renewable materials-based wood adhesives

2.2.2.1 Modifications of renewable-based wood adhesives

Renewable adhesives offer several advantages over synthetic adhesives. However, certain disadvantages exist such as low strength, susceptibility to microbial attack, limitation to dry interior applications and restriction to the joining of low-strength materials. There has been a series of publications on the development of more environmentally friendly wood adhesives from renewable materials, by the incorporation of some chemicals as modifying agents to improve their properties. Renewable materials-based adhesives are usually modified chemically by using crosslinkers and hardeners such as, wax, glyoxal, alkali, polyamide-amino-epichlorohydrin, paraformaldehyde, glutaraldehyde (GA), or polymeric methylene biphenyl diisocyanate (PMDI) (Wang et al., 2011; Bertaud *et al.*, 2012; Chen et al., 2012; Santoni , 2013). Ackar et al. (2010) buttress the point by stating that undesirable properties of native starch could be overcome by crosslinking reaction with crosslinking agents such as epichlorohydrin. Sulaiman et al. (2013) evaluated the properties of particleboard using oil palm starch modified with epichlorohydrin. The authors stated that the particleboard panels produced exhibited mechanical strength that satisfied Japanese Industrial Standards (JIS) but the thickness swelling and water absorption did not meet minimum requirements as stated in the standard. The authors concluded that the use of oil palm starch modified with epichlorohydrin as a binder has the potential to be used as a green adhesive in commercial applications. Dongre et

al. (2015) in their research work on lignin-furfural based adhesives, used lignin recovered from the hot-water extraction of sugar maple to synthesise adhesive blends to replace phenol-formaldehyde (PF) resin. They observed that the adhesive blend prepared at pH of 0.65 with no added furfural exhibits the highest tensile properties and meets 90% of the PF tensile strength. Bertaud et al. (2012) also developed a green adhesive for fibreboard using tannins and lignin from pulp mill residues. In their novel formulations of tannin/hexamine + glyoxylated lignin, they discovered that the internal bond strength of a panel manufactured with 60% tannin/40% lignin satisfied the value required by the European standard.

Furthermore, Ema et al. (2012) reported blending of soy flour (SF), lignin, acetic acid (CH_3COOH) and sodium hydroxide to develop green adhesive and state that adhesive with this formula SF: lignin: CH_3COOH weight ratio of 3: 75: 10 with pH 11 resulted in the highest value of MOR, IB strength and water resistance. The author observed that fibreboard made from lignin-soy based natural adhesive shows promise and possibilities for industrial application in wood composite industries. They concluded that lignin-soy based adhesive produced boards with good mechanical properties without toxic effect to humans. In the same vein, Imman (2001) developed a starch-based wood adhesive system where starch was chemically cross linked with polyvinyl alcohol (PVOH) using hexamethoxymethylmelamine (cymel 303 and 323) as a cross-linking agent with the addition of latex in the production to increase moisture resistance and to give a durable adhesive. Liu and Li (2002) also carried out a research work where soy protein was modified with a functional group found in the marine adhesive protein to produce a soy protein adhesive with desirable bonding properties There is also evidence from research carried out by Kumar et al. (2010) that the synthetisation of soybean protein with alkali and protease enzymes will significantly improve the strength and water-resistance of plywood samples bonded with the modified soy proteins.

Conner (2003) described various methods for opening the starch granules which include heating, alkali treatment, acid treatment and oxidation to modify starch before it can be used as an adhesive. Imman (2001) also used hexamethoxymethylmelamine (cymel 303 and 323) as a crosslinking agent with the addition of latex to develop a starch-based wood adhesive system. Epichlorohydrin was used as a crosslinker in the production of wood adhesive from oil palm starch (Sulaiman et al. 2013).

Lignin can be crosslinked either intra- or inter-molecule by either condensation or oxidative coupling to get modified. Lignin can also be cross linked with itself by the addition of sulphuric acid, hydrogen peroxide or via enzymatic means. The Ashland/Hercules Soyad system also used a cross-linking agent such as polyamide-epichlorohydrin (PAE) to modify soy protein (Langenberg et al. 2010).

Lignosulphonates and Kraft lignin are reported to lack active sites and this results in low reactivity requiring longer curing times (Dongre *et al.*, 2015). Raship and Vasile (2007) reported the coupling of epichlorohydrin to give lignin polymers capable of acting as adhesives. Lignin is also used as a hardener to cross link vegetable oils and can also be cross linked through enzymatic coupling reaction. Polyketone is used to modify protein extracted from Jatropha (Hamarneh, Heeres, Broekhuis, and Picchioni, 2010). It can also be modified by blending two or more renewable binders to get the desired properties. For instance, soy protein isolate (SPI) and wheat gluten (WG) can be combined. Combination of tannins and lignin, lignin and furfural, tannins and cornstarch have been investigated in various applications (Moubarik, *et al.*, 2010; Bertaud *et al.*, 2012; Dongre *et al.*, 2015).

2.2.3 Inorganic binders

Inorganic binders, which are commonly used for composite product manufacture, include ordinary Portland cement, phosphate-based and geopolymer binder. Ordinary Portland cement is the most widely used in the wood-cement composite industry. It has high compressive strength and low tensile strength. There are various disadvantages that are associated with the use of Portland cement such as the intensive energy requirement for the production of its raw materials, emission of greenhouse gases and high cost implication due to energy requirement (Bondar et al., 2011). The main drawback associated with ordinary Portland cement is its enormous adverse impact on the environment (Chen et al., 2014). Cement is a brittle material, which propagates cracks easily, however the presence of fibres delays post-yield cracking behaviour.

Due to the aforementioned drawbacks, geopolymers are believed to offer less carbon footprint and are resistant to many durability agents that can plague conventional concrete. They are a cementitious material that are produced by reacting solid aluminosilicates with an alkaline metal solution at ambient or slightly elevated temperature (Wanjari and Sebastian, 2015). They are made from utilisation of waste materials such as kaolin, volcanic ash, fly ash, blast furnace slag, and mine tailings (Joy and Mathew, 2015). This material is being used in various applications to fully or partially replace ordinary Portland cement. Joy and Mathew (2015) used foundry sand as a partial replacement for fine aggregate in geopolymer concrete. The authors used different ratios ranging from 0 to 25% by weight of fine aggregate to replace foundry sand. Compressive strengths of samples were determined after the third and seventh day and it was concluded that there was a decrease in the workability of the samples with increase in foundry sand content. There was also an attempt to examine the suitability of replacing the 30% of fly ash and 50% of artificial sand for a concrete of grade M35. The authors evaluated compressive strength of the concrete for 7 days, 28 days and 56 days of curing period and measured durability characteristics such as Acid Attack Test, Acid Durability Factor, and Acid Attack Factor of

Concrete Mix for 30 days, 60 days, and 90 days. The authors discovered that the results obtained for combined mix were almost equal to those of the conventional mix, therefore recommended that both fly ash and artificial sand combined are suitable replacements for ordinary Portland cement at appropriate mix ratio (Chandana and Shammen, 2015).

Phosphate-based binders were originally used in the development of chemically bonded phosphate ceramics (CBPCs) through acid/base reactions between an acid phosphate and a metal oxide (Wagh et al., 2003). CBPC is a potential inorganic binder for developing wood composite products and various value-added products using huge volume of industrial waste available abundantly around, such as waste paper and pulp mill residues (Laufenberg and Matt 2004). The unique advantage of these binders is emission of low carbon dioxide compared with Portland cement. They are not affected by the sugars and hemicelluloses present in wood and this gives way for wider stream utilisation of wood species (Amiandamhen et al., 2016). The drawback associated with this binder is the high cost of production materials; however this challenge is being addressed by incorporating filler such as ash, in order to reduce the price. A wide range of phosphate binders can be formulated by an understanding of stoichiometry and chemistry of reactions between acids and bases. Examples of phosphate binders include magnesium phosphate and calcium phosphate binders. The former is formulated through the reaction of magnesium oxide (MgO) and monopotassium dihydrogen phosphate (KH_2PO_4) (Wagh, 2013) while the latter can be formulated by the reaction of calcium oxide (CaO) and KH_2PO_4 (Wagh et al., 2003). Phosphate binder can be used in various ways such as adhesive, cement, or surface material to manufacture wood and fibre-based composites.

2.3 Adhesives properties

Adhesives characterisation can be defined as their qualitative and quantitative analysis and it plays a very important role to determine various essential properties of the adhesive such as functional groups, thermal stability and structural stability. The two main methods used to determine adhesives' characteristics are based on chemical method and spectroscopic analysis. Chemical analysis methods are simple and cheap but labour intensive and their usage has been decreasing over time. Spectroscopic methods for characterisation of adhesive systems include Fourier transform infrared (FTIR), Raman spectroscopy, nuclear magnetic resonance (NMR), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and dynamic mechanical thermal analyser (DMTA). The spectroscopic analytical techniques are briefly described in the following subsections.

2.3.1 Fourier transform infrared (FTIR)

FTIR spectroscopy is used to identify functional groups which facilitate adhesion which are present in the adhesives' formulations. Kalami et al. (2017) formulated a 100% lignin-based

resin using an unmodified lignin and FTIR analysis was used to analyse molecular structures of both original and isolated lignin as shown in Figure 3. It was reported that the appearance of relatively intense absorption band at 1694 cm^{-1} (C=O stretching, unconjugated lignin) in conjunction with absence of peak at 667 cm^{-1} (β-glycosidic ethyl linkages polysaccharides) in the isolated lignin could be due to potential breakage of β-glycosidic ethyl linkages between hemicelluloses and lignin during the isolation process. The effects of treatment temperature on the properties of starch-based adhesives developed by hydrolysing starch with polyvinyl alcohol under alkaline and acidic conditions at various treatment temperatures was also analysed through FTIR. It was reported that the treatment with acid and alkali broke the molecular interaction and increased the number of free hydroxyl groups in the adhesives' formulation (Yu et al. 2015). Furthermore, FTIR spectroscopy was used to investigate the effects of modifiers on the bond strength of plywood produced using whey protein-based adhesives. The authors reported that FTIR could not detect effectively the variations of chemical structures related to the crosslinking reaction of these modifiers due to low contents of modifiers (Wang et al. 2011).

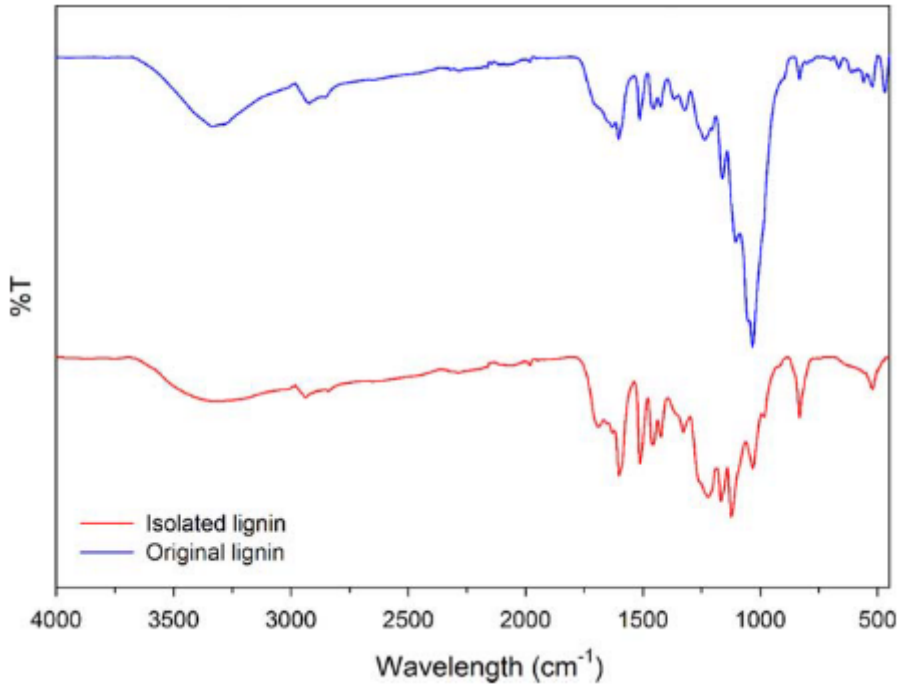


Figure 3: ATR-FTIR spectra of original and isolated lignin sample (Kalami et al. 2017)

2.3.1 X-Ray Diffractometry (XRD) analysis

X-Ray Diffractometry (XRD) analysis is conducted to determine the crystallinity index of an adhesive and manufactured composite panel. Step scan measurements are usually carried out using X-rays (Cu-Kα) generated at the opening voltage and current of 40 kV and 30 mA, respectively. The scan is made from a diffraction angle of 2θ ranging from 10° to 40°,

corresponding to a scanning speed of 0.02° and 2°/min. The crystallinity index (CrI) is calculated using the formula (Eq. 1),

$$CrI\ (\%) = (I_{200}-I_{am})/I_{200} \times 100 \quad (1)$$

Where I_{200} is the peak intensity of the crystalline fraction and I_{am} is the peak intensity of the amorphous fraction (Sulaiman et al. 2013).

The diffraction and crystallinity patterns of adhesives developed from corn-starch under alkaline and acidic conditions at various treatment temperatures were investigated via XRD analysis. It was observed that the peak at 2θ = 17.10° became weaker after treatment while the peak at 2θ = 18.06° became stronger as a result of acid hydrolysis which occurred first in the amorphous chains (Yu et al. 2015). XRD analysis was also employed to evaluate the crystallinity of the materials inside the particleboard produced using modified starch as binder. It was observed from the XRD spectrum shown in Figure 4 that the powder of glutaraldehyde modified cornstarch was highly amorphous and major intensity peaks at 2θ which was observed near 23° related to their crystalline structure (Amini et al. 2013a). Likewise, Sulaiman et al. (2013) used XRD analysis to determine the crystallinity index of starch and manufactured panel made using Oil palm starch modified with epichlorohydrin. It was revealed through X-ray patterns that the crystallinity index of the starch was reduced after the modification process. It was also observed that the panel that had the lowest crystallinity index had better physical and mechanical strength.

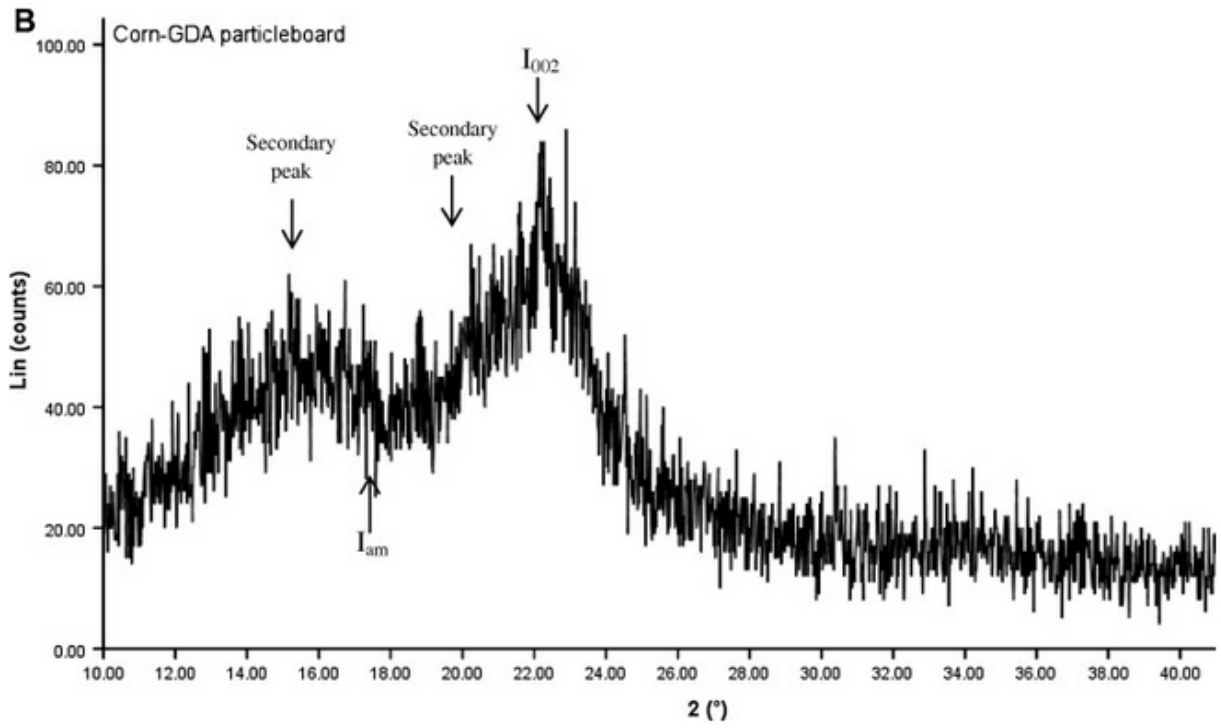


Figure 4: X-ray diffraction spectra of glutaraldehyde modified starch particleboard sample (Amini et al. 2013b)

2.3.2 Thermogravimetric Analysis (TGA)

TGA is used to show how the mass of an adhesive is altered due to changes in temperature or time. This happens because of the degradation of sample material, removal of moisture or oxidation of components. It is valuable in characterising the materials with the original sample and their properties. Its technical characteristics are in two ways, quantitative and qualitative. For quantitative it does the following: monitors mass regarding change in temperature, it measures information about thermal stability, decomposition kinetics, oxidation, loss of water or solvent and weight percentage of ash. When used for qualitative analysis, it can reveal sample components and characteristic dissociation temperatures (Crouch et al 2007). Moubarik et al.,(2010) reported that TGA can be used to check the thermal decomposition and thermal stability of adhesives. Studies by Yu et al., (2015) used thermogravimetric analysis to determine thermal behaviour of cornstarch and treated starch. The authors observed from the curve presented in Figure 5 that there were two weight losses based on temperature. The first weight loss was at a temperature close to 100 °C and minimal while the second weight loss was significant and occurred between 255 and 470 °C. It was further revealed that initial degradation temperatures of treated samples were lower than those of untreated starch. In another study, thermal decomposition curves of polyurethanes from cardanol-furfural were studied. The hard segment polyurethanes showed three exotherms; the weak exotherms and two strong exotherms. The authors reported that hard segment polyurethanes showed a lesser number of

exotherms in comparison with those of the soft segment polyurethanes as a result of higher crosslink density (Gopalakrishnan and Sujatha, 2010).

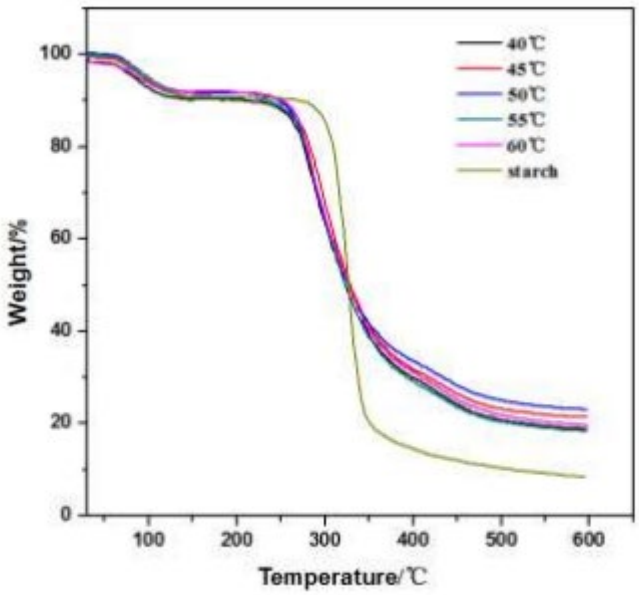


Figure 5: TGA curves of starch and treated starch samples (Yu et al. 2015)

2.3.3 Differential Scanning Calorimetry (DSC)

This technique is used to determine the melting temperature (Tm) and curing temperature (Tc) of adhesive formulation. Kalami et al (2017) used DSC analysis to determine the curing temperature of the phenolic adhesives. The DSC thermosetting graphs showed that main exothermic curing peak of commercial adhesive occurred at 195 °C while that of lignin-based adhesive was at 203 °C. The authors also reported that energy required to cure the lignin-based adhesive is 90 J/g while that of commercial phenol resorcinol formaldehyde is 171 J/g. It was recommended that different additives could be tested to further reduce the curing temperature of the developed lignin-based adhesive. Sulaiman et al.(2013) used DSC analysis to determine the melting temperature (T_m) of particleboards produced using Oil palm starch modified with epichlorohydrin. It was observed that the melting temperature of starch was increasing as the starch was being modified. DSC analysis was also used to evaluate the thermal behaviours of the manufactured particleboards produced using modified starch as binder. The results showed the highest endothermic peaks to be 8.63 mW, at temperature of 92 ^oC, which indicated the melting temperature of the particleboard (Amini et al. 2013b).

2.3.4 Scanning Electron Microscopy (SEM) analysis

This analysis is carried out to determine the compactness and effect of adhesive dispersion or agglomeration of particles in manufactured composite panels. The morphologies of the fracture

surfaces of whey protein-based adhesives were analysed through SEM. The micrograph showed that the fracture surface of cured whey protein adhesives appeared microscopically rough and corrugated like alternating ridges and grooves (Wang et al. 2011). SEM was engaged by Yu et al. (2015) to see to dispersion of both unmodified starch and treated starch samples in the bonded plywood. The micrograph presented in Figure 6 showed that the untreated cornstarch contained dispersed or agglomerated particles that were irregular polyhedrons with smooth surfaces. It also revealed that the surfaces were corroded when the starch was treated with acid and alkali. Imman et al. (2001) used SEM to analyse the visibility of microbial growth on the surfaces of adhesive joints scraped from wood samples bonded with modified starch and exposed for two months at 97% RH followed by one year exposed to 50% RH at room temperature. The result was affirmative. Amini et al. (2013b) also employed SEM technique to see the interaction and distribution of the adhesive developed from modified starch between the particleboard made from rubberwood particles.

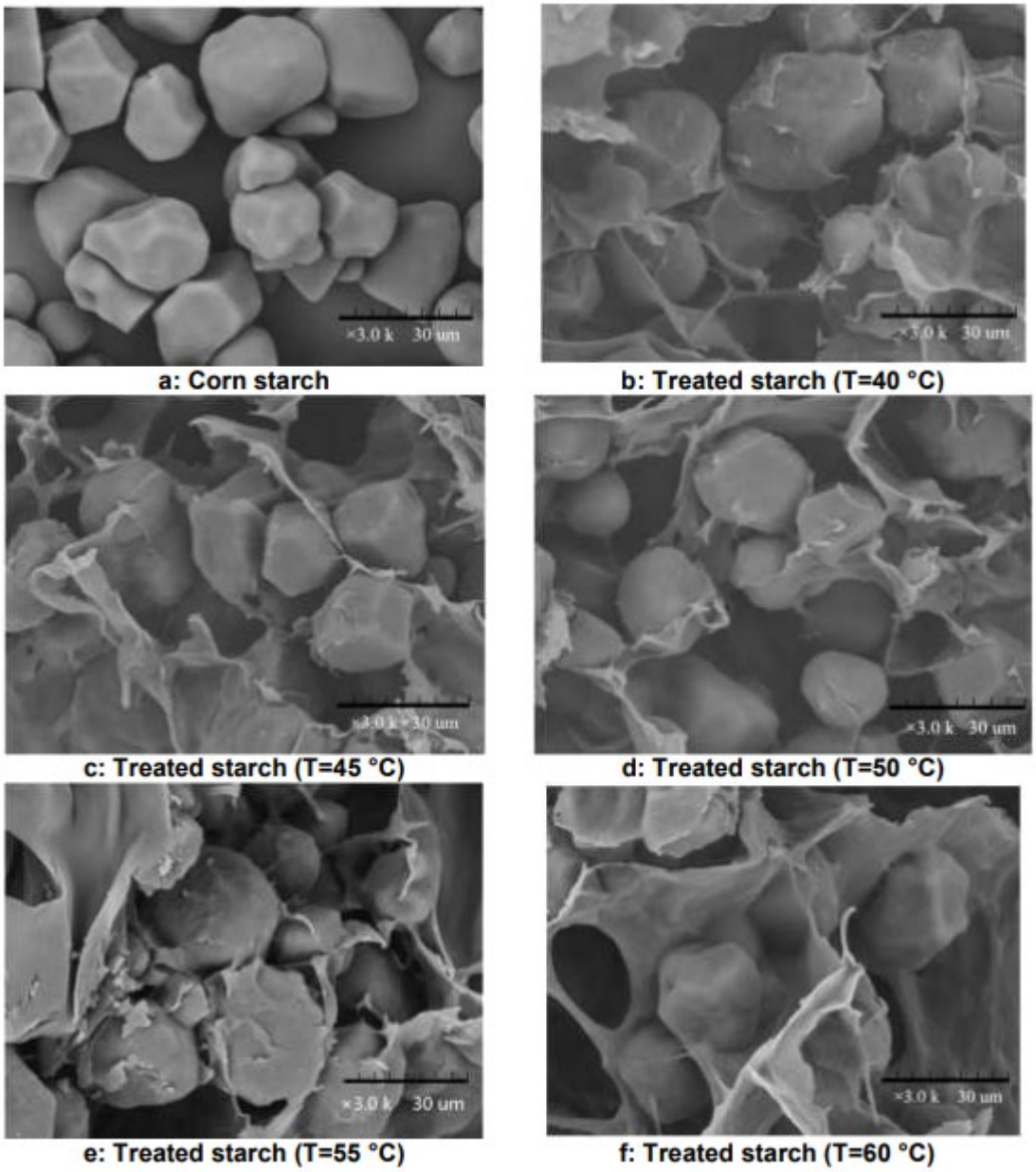


Figure 6: Scanning electron micrographs of cornstarch and treated samples (Yu et al. 2015)

2.3.5 Nuclear Magnetic Resonance (NMR) spectroscopy

NMR spectroscopy is an analytical chemistry technique used in quality control and research for determining the content and purity of a sample as well as its molecular structure. For instance, NMR can quantitatively analyse mixtures containing known compounds. There are different types of NMR spectroscopy. These include ^{13}C NMR, ^{1}H NNR / P NMR, and 2D NMR (HSQC and HMBC). This technique is also used to indicate the difference between NMR spectra of various components in the adhesive. In their study, Moubarik et al. (2010b) used ^{13}C NMR to compare the molecular weight compounds of cornstarch, NaOH/cornstarch, mimosa tannin/hexamine and cornstarch-NaOH-MT-H adhesive. The comparative ^{13}C NMR spectra of

cornstarch and NaOH/ cornstarch presented in Figure 7 show that some low molecular weight compounds were produced, and this was established due to the emergence of new peaks. ^{1}H-NMR was used to confirm the chemical structure of grafted starch, the structures of gelatinised starch and copolymer and It was established through the spectroscopy, the characteristic proton peak of starch as well as the new proton signal that indicated the formation of the grafted copolymers (Wang et al. 2012). Figure 7 shows comparative solid state CP-MAS 13C NMR spectra of cornstarch, NaOH/cornstarch, mimosa tannin/hexamine and cornstarch/NaOH/mimosa tannin/hexamine.

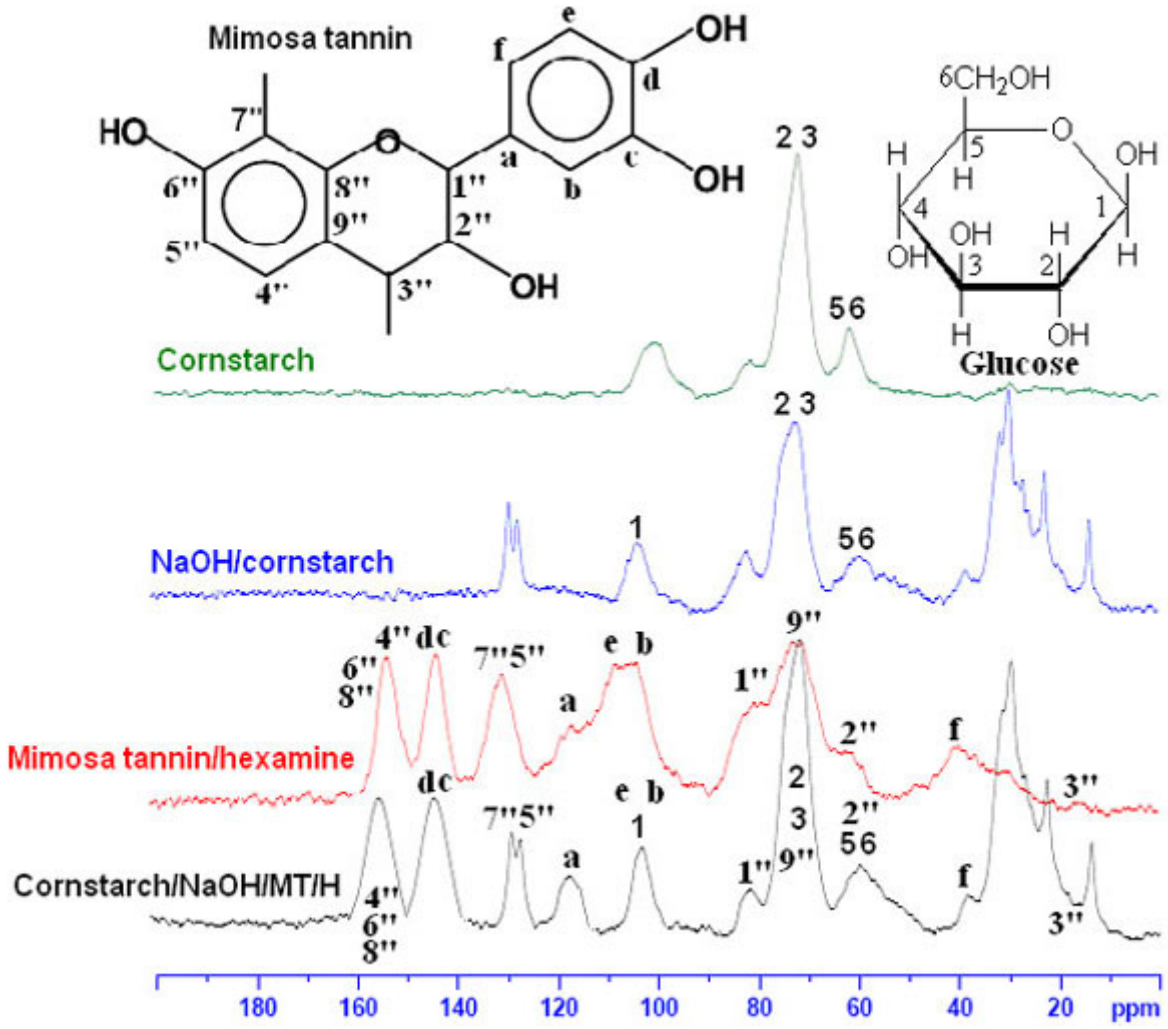


Figure 7: Comparative solid state CP-MAS 13C NMR spectra of cornstarch, NaOH/cornstarch, mimosa tannin/hexamine and cornstarch/NaOH/mimosa tannin/hexamine (Moubarik et al. 2010b)

2.4 Mechanism of adhesives production

Adhesives are developed by mixing the base materials which may be of natural or synthetic origin with fillers, catalysts or hardeners, accelerators, inhibitors, retarders, solvents, diluents, extenders, fillers, carriers and reinforcements, plasticisers, tackifiers, thickeners and thixotropic agents, film formers, antioxidants, antihydrolysis and antifungal agents, surfactants, wetting agents, pigments, stabiliser and other additives (Petrie, 1999). Selection of the adhesive components depends on the factors such as end-properties required, application and processing requirement, and the overall cost target. Industrial manufacturing processes for the majority of the wood-based materials in use today largely depend on adhesives and the physicochemical phenomenon of adhesion (Sulaiman et al.,2013).

2.5 Seed-based adhesives

Natural-based adhesives are long, straight or branched chain polysaccharides that contain hydroxyl groups, which bond to water molecules. They are widely available and generally non-toxic (Ikechukwu and Salome 2013). These adhesives can be obtained from various sources, such as locust bean, guar, tamarind, xanthan and *Irvingia* kernel extract; and they belong to the group of polysaccharides (Norström et al. 2014). There has been limited research concerning wood adhesives based on seed gums. Haag et al. (2004 and 2006) evaluated the possibilities of using extracellular microbial polysaccharides derived from bacteria and reported successful results with dry bond strengths comparable to a poly (vinyl acetate)-based adhesive.

2.6 Study Species (*Irvingia*)

Irvingia wood species have been earmarked for domestication in many countries of the world due to their potential as raw materials for various applications, which include biodiesel, cosmetics, perfume and soap. This section discusses the product development, composition, trade analysis and uses of *Irvingia* species.

2.6.1 Product development

Irvingia adhesives could be readily made from extract of *Irvingia* species plant. There are few publications on the evaluation of *Irvingia* extract's potential bonding properties. It had been mainly investigated for the pharmaceutical industries as a drug binder (Ikechuckwu and Salome, 2013; Eraga, 2014) while its binding ability is yet to be explored in the wood composite industry. Figure 8 gives an overview of product development from seeds of *Irvingia* species [*Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW)].

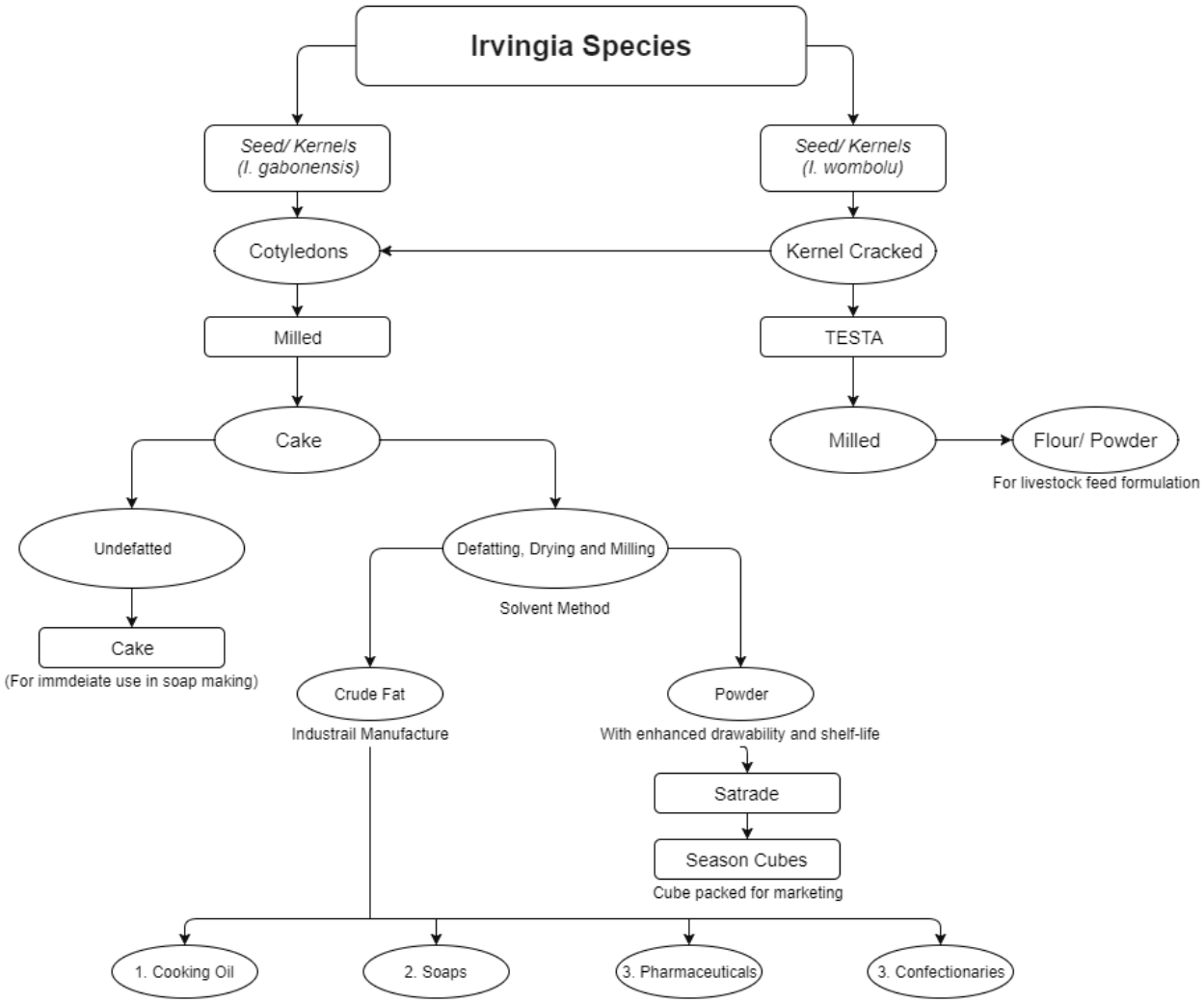


Figure 8: Product development from seeds of *Irvingia* species

2.6.2 Composition

Ikhatua et al., (2012) analysed the essential oil components of IG and IW from Southern Nigeria and reported that twelve and ten components were identified in IG and IW respectively, of which carboxylic acids and esters were the major components in both species. They reported that fatty acids and esters were the most abundant components in the oils. Table 2 shows values from physicochemical characteristics of *Irvingia* kernels by various authors. Most authors did not differentiate between the species during the analysis. The values reported by authors for the same *Irvingia* element were different and these may be due geographical variation.

Table 2: Physicochemical characteristics of *Irvingia* kernels

Elements	Value	References
Total carbohydrate (%)	26.0[1],18.7[2a],62.3[2b],19.0[3],39.2[4a],41.0[4b]	Ejiofor et al., (1987)[1]; Ikhatua and Falodun (2012)[1]; Ogunshina et al., (2012)[2 & 7]; Achinehwu (1998)[3]; (Ikhatua Iyayi Matilda and and Falodun Abiodun 2012)Ikhatua et al., (2012)[3], Ikhatua (2010)[4], Awono et al., (2002)[5 & 6]; Ewane (2010)[5 & 6]; FAO (2007)[5 & 6].
Crude protein (%)	7·4[1],8.9[2a],25.2[2b],8-11[3], 9.2[4a], 9.7[4b],7.5[5],8.0[6]	
Ash (%)	2.5[1],2.3[2a],6.2[2b],1-3[3],2.1[4a],2.3[4b]	
Crude fibre (%)	0.9[1],8.2[3],9.8[4a],8.6[4b]	
Vitamin (mg/100g)	9.2[1]	
Vitamin A (mg/100g)	0.6[1]	
Fat (%)	51.3[1],68.4[2a],39.7[4a],38.4[4b]	
Moisture (%)	2.5[2],5.1[5]	
Ether extract (%)	55-70[3]	
Colour intensity (Lovibond units)	3.4[7]	
Free fatty acids	2.72 g/100mg[7]	
Peroxide	0.5 meg 0_2/kg[7]	
Iodine	8.2g I_2/100_g[7]	
Saponification	256.5mgKOH/100g[7]	
Carbohydrate (NFE)	39.2%[4a],41.0[4b]	
Calories (Kcal)	670.0[5],706.0[6]	
Lipids (g)	68.9[5],73.0[6]	

Glucides (g)	18.6[5],17.0[6]	
Calcium (mg)	126.0[5],133[6]	
Iron (mg)	3.4[5],4.0[6]	

2.6.3 Uses

Joseph (1995) listed the potential industrial applications of bush mango kernel fat, including cooking oil, margarine, perfume, soap and pharmaceuticals. The author observes that once the fat has been extracted from the kernels, the residue still possesses the consistency and thickening properties essential for soup-making, so there are no wasteful byproducts from the fat extraction process; both the fat and the residue can be used. Aside from its role as a thickener, the residual kernel cake could also be used as a binder in food or pharmaceutical products (Ikechukwu & Salome, 2013). Ndjouenkeu (1996) extracted the polysaccharides from *Irvingia* kernels and analysed their properties. The author concluded *Irvingia* kernels have potential to be used as an industrial gum. Ogunsina et al. (2012) reported that the fatty acid composition showed a rich presence of myristic acid and a substantial amount of lauric acid and this could be exploited to promote it as a potential source of myristic acid with additional benefit of medium chain lauric acid. Figure 9 shows distribution of IG and IW across West and Central African countries.

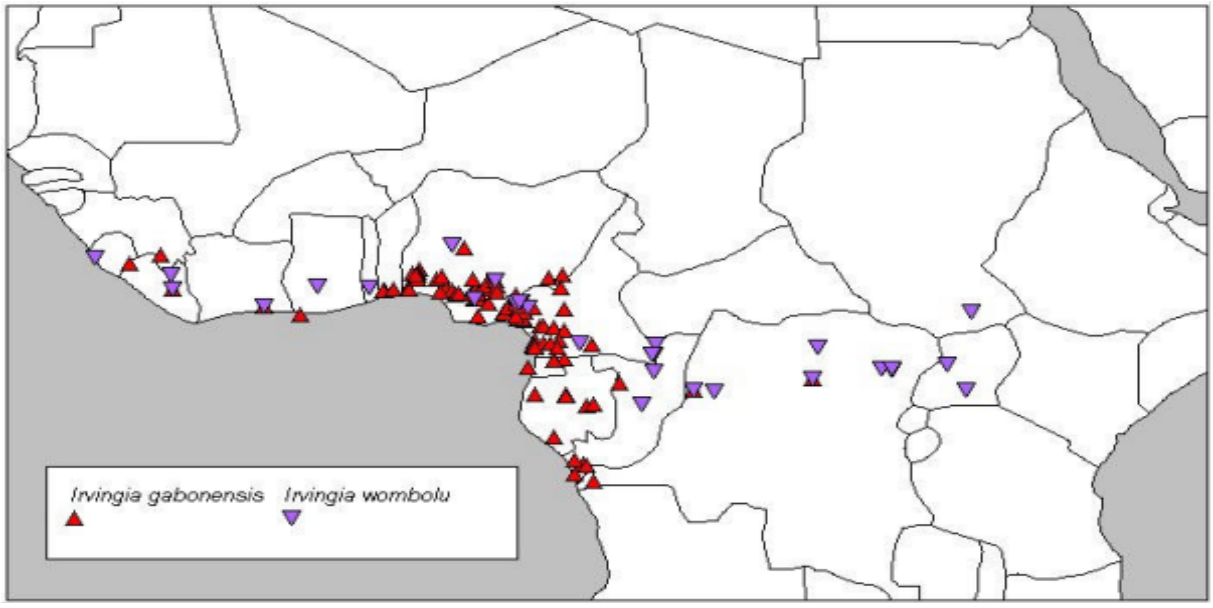


Figure 9: Distribution of *Irvingia gabonensis* and *Irvingia wombolu* in Central and West Africa (Ainge & Brown, 1998)

2.6.4 Trade analysis

At present, IG and IW are widespread in West and Central Africa and not endangered, even though its natural habitat is being cleared for agricultural land and its products are often overexploited. Market assurance for *Irvingia* products will encourage farmers into greater cultivation of the species. It is possible that if many farmers begin to produce *Irvingia* products on a large scale, then supply would exceed demand and prices would fall (Ainge & Brown, 1998). Figure 10 shows pictures of unripe *Irvingia* fruits.

Figure 10: Unripe *Irvingia* fruits

Irvingia markets extend from local and regional to international levels and there is even inter-continental export. According to Ewane (2010) findings on markets and market chain analysis for bush mango (*Irvingia* species) in the Southwest and East regions of Cameroon, revealed an estimated annual exports from the Southwest region at 1 470 tones. The author stated that prices of bush mango vary from one season to another. Awono et al., (2002) and Ewane, (2010) revealed that the quantity of IG exported to Nigeria was 2 400 tonnes and 302 tonnes was exported to Equatorial Guinea and Gabon in 2007 from Central, South and Littoral Regions of the humid lowlands of Cameroon. They also reported that over USD2 million was spent to export the species from Nigeria and Central Africa to the United Kingdom and Belgium in 1999. Ndoye et al., (1998) and Ewane (2010) reported that the total value of sales of bush mango was 34,633,100 CFA francs (USD70,000) in 28 markets in the humid forest zone (HFZ) of Cameroon over 29 weeks. The price of *Irvingia* kernels varies and fluctuates with seasonal availability and location. Presently the price of 1 kg of dried kernels is USD16.6 in Nigeria, USD20 in Gabon, and USD27.1 in India. Figure 11 shows photos of dried kernels of *Irvingia* species.

Figure 11: Dried kernels of *Irvingia* species

2.7 Conclusion

There has been increased interest in the environment over the last few years. One of the ways to ensure an environmentally benign ecosystem is through the production and use of renewable adhesives for the manufacture of reconstituted and engineered wood. Although there are several advantages that renewable materials-based adhesives offer compared to synthetic adhesives, certain disadvantages such as low strength, susceptibility to microbial attack, limitation to dry interior applications and restriction to the joining of low strength materials limit their utilisation. These shortcomings can be overcome by modification with different materials such as hardeners and crosslinking agents to get desirable properties.

Chapter 3

Material and methods

3.1 Material

The materials used in this study were *Irvingia* kernels, wood particles and veneers. The kernels were from *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW) species and they were purchased from Enugu State, Nigeria. The wood particles were from dried slash pine (*Pinus elliottii*) supplied by Cape Pine SA, a local subsidiary of the Global Environment Fund (GEF). This was supplied as waste from processed logs. Veneers were also from (*Pinus elliottii*) and supplied by York Timber, South Africa. Bondtite resin was supplied by Bondtite (PTY) Limited, South Africa.

3.2 Reagents

The following chemicals were used in this study: Analytical grade Epichlorohydrin (≥ 99%), Glyoxal solution (40 wt.% in H_2O), Glutaraldehyde solution (Grade II, 25% in H_2O), and Hydrochloric acid (37%), Petroleum ether, Sodium chloride, Sodium metabisulphite, Hexamine and Dicyandiamide (99%) were supplied by Sigma-Aldrich Pty. Ltd., SA. Sodium hydroxide (97%) was supplied by Science World Company SA. Sodium metabisulphite and sodium chloride were purchased from Associated Chemical Enterprises, South Africa.

3.3 Methods

3.3.1 Chemical analysis

The kernels for both species were air dried in a greenhouse for 14 days. Thereafter, they were milled using a hammer mill fitted with a 1 mm sieving slice. The obtained particles from the kernel and dried kernel extracts from different extraction methods were analysed for protein, fat, ash and carbohydrate content using Association of Official Analytical Chemists Methods (AOAC Methods. 2005).

PROTEIN DETERMINATION

According to this standard, the protein content of the samples was determined by the Kjeldahl technique. This consists of three techniques of analysis namely Digestion, Distillation and Titration.

Digestion

An amount of 0.5 g of each finely ground dried sample was weighed carefully into the Kjeldahl digestion tubes to ensure that all sample materials got to the bottom of the tubes. To this 1 Kjeldahl catalyst tablet and 10 ml of Concentrated H_2SO_4 were added. These were set in the appropriate hole of the Digestion Block Heaters in a fume cupboard. The digestion was left on for 4 hours, after which a clear colourless solution was left in the tube. The digest was cooled and carefully transferred into a 100 ml volumetric flask, thoroughly rinsing the digestion tube with distilled water and the flask was made up to mark with distilled water.

Distillation

The distillation was done with Markham distillation apparatus which allows volatile substances such as ammonia to be steam-distilled with complete collection of the distillate. The apparatus was steamed out for about ten minutes. The steam generator was then removed from the heat source to all the developing vacuum to remove condensed water. The steam generator was later placed on the heat source (i.e. heating mantle) and each component of the apparatus was fixed up appropriately.

Determination: A 5 ml portion of the digest above was pipetted into the body of the apparatus via the small funnel aperture. To this was added 5 ml of 40% (W/V) NaOH through the same opening with the 5 ml pipette.

The mixture was steam-distilled for 2 minutes into a 50 ml conical flask containing 10 ml of 2% Boric Acid plus mixed indicator solution placed at the receiving tip of the condenser. The Boric Acid plus indicator solution changes colour from red to green showing that all the ammonia liberated has been trapped.

Titration

The green-coloured solution obtained was then titrated against 0.01N HCL contained in a 50 ml Burette. At the end point or equivalent point, the green colour turns to wine colour which indicates that all the Nitrogen trapped as Ammonium Borate $[(NH_4)_2BO_3]$ has been removed as Ammonium chloride (NH_4CL).

The percentage nitrogen in this analysis was calculated using the formula:

% N = Titre value x Atomic mass of Nitrogen x Normality of HCL used x 4

or % N = Titre value x Normality/Molarity of HCL used x Atomic mass of

N x Volume of flask containing the digest x $\frac{100}{1}$

Weight of sample digested in milligram x Vol. of digest for steam distillation. The crude protein content was determined by multiplying percentage Nitrogen by a constant factor of 6.25 i.e. % CP = % N x 6.25.

FAT DETERMINATION

For this, 1 g of each dried sample was weighed into a fat-free extraction thimble and plugged lightly with cotton wool. The thimble was placed in the extractor and fitted up with reflux condenser and a 250 ml soxhlet flask which has been previously dried in the oven, cooled in the desiccator and weighed. The soxhlet flask is then filled to $^3/_4$ of its volume with petroleum ether (b.pt. 40 ºC–60 ºC), and the soxhlet flask, extractor plus condenser set was placed on the heater. The heater was put on for six hours with constant running water from the tap for condensation of ether vapour. The set was constantly watched for ether leaks and the heat source was adjusted appropriately for the ether to boil gently. The Ether was left to siphon over several times say at least 10–12 times until it was short of siphoning. After this if any ether content remained in the extractor it was carefully drained into the ether stock bottle. The thimble containing the sample was then removed and dried on a clock glass on the bench top. The extractor, flask and condenser were replaced and the distillation continued until the flask was practically dry. The flask which now contains the fat or oil was detached, its exterior cleaned and dried to a constant weight in the oven. If the initial weight of the dry soxhlet flask is Wo and the final weight of oven dried flask + oil/fat is W_1, percentage fat/oil was obtained by the formula:

$$\frac{W_1 - Wo}{\text{Wt. of Sample taken}} \times \frac{100}{1}$$

MOISTURE DETERMINATION

For this, 2 g of the sample was weighed into a previously weighed crucible. The crucible plus sample was then transferred into the oven set at 100 °C to dry to a constant weight for 24 hours overnight. At the end of the 24 hours, the crucible plus sample was removed from the oven and transferred to desiccator, cooled for ten minutes and weighed.

If the weight of empty crucible is Wo

weight of crucible plus sample is W_1

weight of crucible plus oven-dried sample W_3

$$\% \text{ Moisture} = \frac{W_1 - W_3}{W_1 - Wo} \times \frac{100}{1}$$

DETERMINATION OF ASH

For this, 2.0 g of the sample was weighed into a porcelain crucible. This was transferred into the muffle furnace set at 550ºC and left for about 4 hours. About this time it had turned to white ash. The crucible and its content were cooled to about 100 ºC in air, then at room temperature in a desiccator and weighed. This was done in duplicate. The percentage ash was calculated from the formula below:

$$\text{Ash content} = \frac{\text{wt. of ash}}{\text{original wt. of sample}} \times 100$$

CARBOHYDRATE BY DIFFERENCE DETERMINATION

The carbohydrate was determined by difference. This was done by subtracting SUM of (Moisture % + % Crude Protein + % Fat + % Ash) from 100 i.e. (100 – (% M + % P + % F + % Ash).

3.3.2 Extraction

Several methods for extracting the gum from *Irvingia* have been reported. Some of the methods employed in this study using different solvents are described below and compared in terms of efficiency, yield, and properties of the kernel extract.

3.3.2.1 Sodium chloride extraction

This extraction followed the procedure described by Ogaji et al (2012). A sample of 100 g of ground seed of *I.gabonensis* was transferred to a 2 L beaker containing 2 L of 1% w/v sodium chloride preheated to about 78 °C. The mixture was heated on a hotplate to about 78–85 °C. The mixture was mixed gently for an hour with the aid of a magnetic stirrer. The mixture was then left to stand at room temperature (~21 °C) for 24 h. Solidification of the lipids component took place at the top and the bottom of the mixture and the lipids were subsequently removed by filtration through a 105 µm cloth sieve. The lipids were air-dried and stored in an airtight container until ready for use. The remaining sample containing the gum was centrifuged (Allegra 6R centrifuge, Beckman Coulter™, USA) at 3 440 rpm for 10 min to remove other impurities. The resultant clear supernatant mucilage (kernel extract) was dried in a lyophiliser and stored in an airtight container until required for further analysis.

3.3.2.2 Water extraction

Water extraction was carried out according to the method reported by Eraga et al. (2014) with slight modification. According to the method, 100 g of the powdered cotyledon of *Irvingia gabonensis* and *Irvingia wombolu* was dispersed in 2 L of distilled water in a plastic container. The mixture was mixed gently for 1 h with the aid of magnetic stirrer. The dispersion was homogenised for about 1 h and left for 24 h. The mucilage formed was then filtered through a clean muslin cloth to obtain a viscous filtrate (gum). The filtrate was centrifuged at 3440 rpm for 10 min to separate the fat. The supernatant mucilage (kernel extract) gum was then dried in a lyophiliser. The resulting powder was kept in an airtight container until required for further analysis.

3.3.2.3 Sodium metabisulphite extraction

This extraction was carried out according to the methodology developed by Ikechukwu and Salome (2013) with slight modification. 100 g of the powdered cotyledon of *Irvingia gabonensis* and *Irvingia wombolu* kernels was soaked in 2 L of distilled water containing 1% sodium metabisulphite for about 12 h. Thereafter, it was filtered, and the gum was centrifuged at 3 000 rpm for 10 min to separate the fat. The supernatant mucilage (kernel extract) was then dried in a lyophiliser. The resulting powder was kept in an airtight container until required for further analysis.

3.3.3 Extract yield

This was carried out according to the method employed by Razavi et al (2009). The yield from different extraction methods for the two species was determined by weighing the dried *Irvingia* extract and calculated on wet basis.

3.3.4 Physical properties

3.3.4.1 Specific Gravity

The specific gravity (S) of the *Irvingia* adhesives was determined by dividing the weight of the resin by the weight of an equal volume of water according Çetin and Özmen (2003).

$$\text{Specific gravity} = \frac{\text{Resin weight (g)}}{\text{weight of an equal volume of water (g)}} \quad [1]$$

3.3.4.2 pH

The pH of all the *Irvingia* adhesives was measured with a digital pH meter (Mettler Toledo S220) according to Kalami et al. (2017).

3.3.5 Adhesive characterisation

3.3.5.1 Thermogravimetric analysis (TGA)

TGA analysis was carried out according to the method reported by Sulaiman et al. (2013). The thermal stability of the *Irvingia* extract powdered samples and subsequent modified samples were analysed using a TGA Q50 thermogravimetric apparatus. Approximately 5 mg of each powdered sample was placed on a balance located in the furnace and heat was applied over the temperature range from room temperature to 800 °C at a heating rate of 20 ^{0}C/min in a nitrogen atmosphere. The derivatives of the weight loss vs. temperature thermograms were obtained to show the different decomposition processes.

3.3.5.2 Differential Scanning Calorimetry (DSC) analysis

The melting temperature (T_m) of each *Irvingia* extract and modified samples were determined using a TA Instruments Q100 calorimeter. This was done according to the procedure outlined by Ahire et al. (2016). The instrument was calibrated with an indium metal standard according to standard procedures. About 4 mg of the powdered samples was put into an aluminium pan, with the usage of empty pan as reference. The samples were heated up at a rate of 10 °C/min within the temperature range of -15 °C and 150 °C under inert nitrogen atmosphere. A constant ramp rate of 10 °C/min was used for both heating and cooling cycles.

3.3.5.3 Fourier Transform Infrared (FTIR) spectroscopy analysis

The *Irvingia* extract and subsequent samples were analysed using Fourier transform infrared (FTIR) spectroscopy operating in Attenuated Total Reflectance (ATR) mode. This was carried out according to the method described by Naron et al. (2017). The powdered extract samples were pressed against the diamond crystal surface with a spring-loaded anvil of a Thermo Nicolet, Nexus^{TM} model 470/670/870 FT-IR spectrometer equipped with ZnSe lenses. Spectra were collected in ATR mode at a resolution of 4 cm^{-1} and 32 scans per sample within the absorption bands in the region of 4 000–650 cm. Data collection and further processing were carried out in the Thermo Scientific OMNIC software. To distinguish between the spectra pattern exhibited by the different *Irvingia* adhesives samples, Principal Component Analysis (PCA) was performed using Statistica software (Statsoft V12).

3.3.6 Tensile strength test

This was conducted according to the method given by Dongre et al. (2015) with slight modification. Whatman GF/C glass microfiber filter material was used for the experiment. It was cut into 102 × 25.4 mm strips and oven-dried at 105 °C and weighed. 5 g of dried *Irvingia* extract was dissolved in 37 mL of water. The strips were immersed completely in the formulated adhesives for 5 min, removed and left to dry overnight. This procedure was repeated with a

commercial urea resin Bondtite® for comparison. The dried strips were placed on smoothed aluminium foil and covered by another layer of smoothed aluminium foil, to prevent sticking to the caul plates during the hot-pressing stage. The dried strips were then pressed in an electric hydraulic press at a temperature of 150 °C and pressure of 2 MPa in order to cure. Curing is necessary in order to further enhance the adhesive-adhesive and the adhesive-substrate (glass fibre) cross linking reaction (Dongre et al. 2015). The pressed glass fibres were oven-dried again at 105 °C and weighed to determine the amount of adhesive absorbed by the samples. The strips were conditioned at 20 °C ± 2 °C and 65% RH prior to testing. The tensile strength of the strips was measured using an Instron Universal machine (Model 3322), with a cross head speed of 2mm per min and a 5KN load cell. The inert glass fibres do not absorb water and any change in its properties can be attributed to the adhesive rather than to the fibre substrate. The tensile strength of the adhesive was calculated using the formula:

$$T = \frac{T_R - T_B}{M} \qquad [2]$$

Where T = Tensile strength per gram (N/mg), T_R = tensile strength of reinforced fibre (N/m), T_B = tensile strength of the blank fibre (N/m), M = mass of adhesive absorbed by the glass fibre.

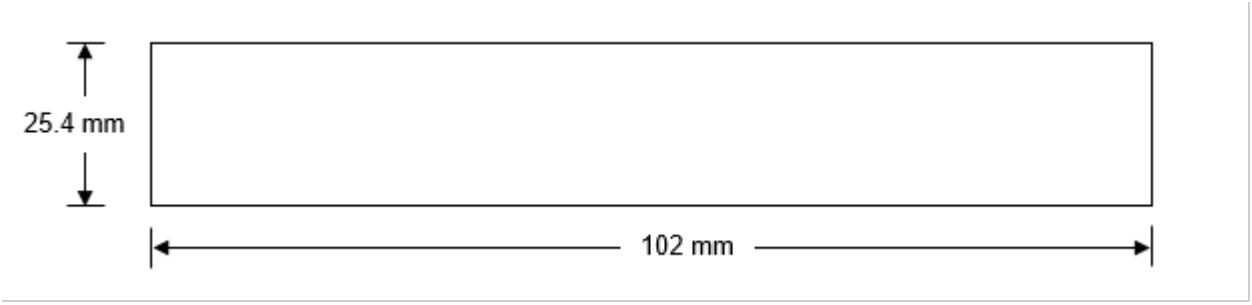


Figure 12: A plan of glass microfibre filter strip

3.3.7 Adhesives modification

This modification procedure was adapted from Imam et al. (2001). Modification of the adhesives was carried out using different hardeners, namely epichlorohydrin, glutaraldehyde and glyoxal to establish the one that resulted in the best performance properties. Hexamine was used as a crosslinker. To prepare 50 g of adhesive, 14.7 g of dried powder extract from each species was dissolved in 27.5 mL of distilled water and was set on a magnetic hotplate stirrer. The hotplate temperature was set at 60 ˚C while the mixture was stirred gently for about 1 h. The solution was cooled to a temperature of 25 ˚C. Then 4.8 mL of each hardener (epichlorohydrin, glutaraldehyde and glyoxal) and 3 g of hexamine were added separately to the solution to produce the binder. Volumes were adjusted for loss of water. Each mixture was continuously stirred for 10 min and then left to cool to room temperature. The acid/base modification was done according to the method employed by Chen et al. (2013). This method involved

modification with acid, salt, dicyandiamide and alkali. According to this method, 200 mL of distilled water was added to 5 g of dried powder extract in a beaker. This was stirred at a speed of 100 rpm at 35 ˚C for 60 min. Then, 0.6 mL hydrochloric acid (37%) solution was added and stirred at 120 rpm for 30 min. Afterwards, 0.2g of dicyandiamide (99%) was added and stirred for another 60 min. Finally, 2 g of sodium hydroxide (97%) pellets were added to the above mixture and stirred for 10 min. The modified samples were freeze-dried for about 23 h, ground into powder and kept in sealed plastic bags for further characterisation and tests.

3.3.8 Shear strength test

The shear strength properties of all the modified *Irvingia* adhesives were determined according to the ASTM D-906-64 test method, which measures adhesive shear strength in a plywood construction by tension loading (Instron Universal testing machine). Three-layer plywood was prepared from pine veneer with length 83 mm, width 25.4 mm and thickness of 3 mm. The two outer veneers were laid alternate to the middle layer. Each veneer was coated with 250 g/m^2 of adhesive and exposed to air for about 15 min to evaporate excessive moisture. Glued veneers were hot pressed at 110 ºC temperature with a pressure of 1.6 MPa for 10min. The test specimens were cut as shown in Fig.13. This was best accomplished by cutting the notches to the proper width, depth, and location in the test panel, using a hollow-ground grooving saw. The notches were cut in the panel in a such a manner so as to ensure that when the specimens were subjected to loading, the lathe checks in the centre ply of half the specimens was pulled open (tension) (see Figure 13a), while in the other half the lathe checks were pulled closed (see Figure 13b). Ten replicates of each sample were prepared. The test specimens were placed in a conditioning room at 65% RH and 20 ºC for 96 h prior to tensile strength testing.

Afterwards, the test specimen was placed in the jaws of the grips in the testing machine so that the specimen was perfectly aligned and parallel to the centreline of the jaws. A test load was applied at a crosshead speed of 5 mm/min. A total of 10 replicates were tested for each treatment.

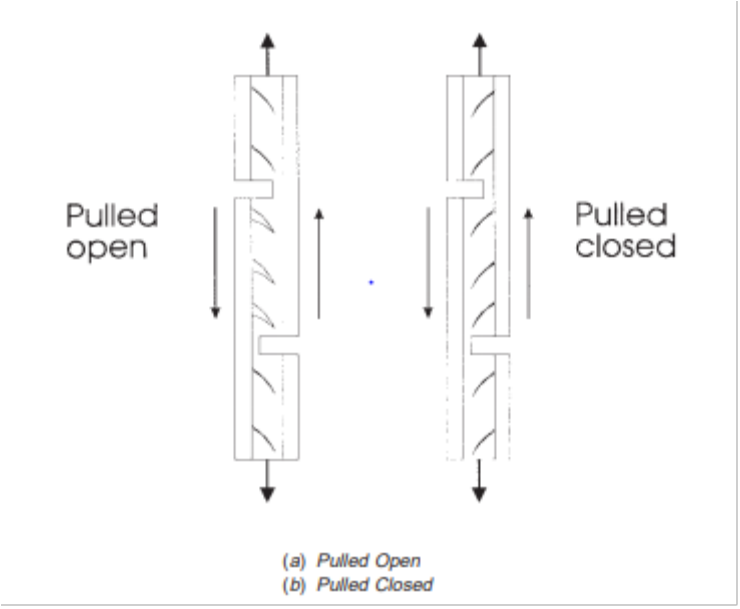


Figure 13: Lathe and notch orientations for testing

3.3.9 Particleboard preparation

The pine particles were milled using a hammer mill fitted with a 1 mm sieving slice. The resultant particles were conditioned at 20 °C and 65% relative humidity (RH) for 96 h. The equilibrium moisture content of the materials was determined as 7%. About 10% of the oven-dried weight of the wood in adhesives were mixed manually with the wood particles. The furnish was poured into a steel mould measuring 218 x 75 x 40 mm and a steel bar 27 mm thick was placed on top. The purpose of the steel bar was to compress the composite in the mould to a final thickness of 13 mm. The set-up was transferred to the laboratory press and a pressure of 200 KPa was applied for 15 minutes at temperature of 165 °C. Thereafter, the mould was removed from the press and the board was de-moulded. The formed boards were thereafter, conditioned at 20 °C and 65% RH for 96 h before testing. Three boards were produced from each *Irvingia* adhesive.

3.3.10 Particleboard evaluation

The properties of the formed panels were evaluated to investigate the effect of modification additives on the flexural strength and dimensional stability of the panels. Flexural test specimens were tested according to ASTM D1037-06a standard using an Instron testing machine fitted with a 5 KN load cell, operated at a rate of 5 mm/min. The specimens were tested to failure and the MOR and MOE were calculated from the formula outlined in ASTM (2006). Samples for dimensional stability were cut using a horizontal bandsaw into dimensions of 75 x 50 mm. The thickness of all samples used in the test was 13 ± 1.2 mm based on the set-up configuration of the steel mould. Water absorption (WA) characteristics and thickness/volume swelling (TS) tests were carried out by submerging conditioned specimens horizontally in fresh water for 24 h. After submersion, the specimens were suspended to drain

for 10 min and excess water was removed from the surface. The specimens were weighed, and the thickness was determined as an average of four measurements. The WA of the specimen was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS of the specimen was calculated as a percentage of the conditioned thickness. Three replicates were used from each treatment for the test.

3.3.11 Statistical analysis

The statistical analysis was performed using STATISTICA (version 13). Analysis of variance (ANOVA) was used to determine if there were significant differences in the extract yield from different extraction methods for the two species. ANOVA was also used to analyse the shear strength of the adhesives in relation to different modification methods and species, in order to determine the effect of modification methods and species on the shear strength of modified *Irvingia*-based adhesives. Panels data were analysed through a post hoc test to evaluate if there were statistically significant differences among panels made with modified adhesive samples. It was also used to determine the effects of modifications on the physical and mechanical properties of the boards.

Chapter 4: Results and discussions

Properties and characteristics of *Irvingia gabonensis* and *Irvingia wombolu* seed kernel extract

4.1 Composition of kernels

The composition of *Irvingia wombolu* and *Irvingia gabonensis* kernels is presented in Table 3. The results agree well with those obtained by Ikhatua et al. (2010), although the values may vary slightly with values reported by some researchers. This may be due to differences in the geographical location of the seed origin and species.

Table 3: Composition of *Irvingia wombolu* and *Irvingia gabonensis* kernels

Species	Carbohydrate (%)	Protein (%)	Fat (%)	Ash (%)	Moisture Content (%)
Irvingia wombolu	21.2 (0.82)	6.5 (0.36)	67.5 (1.69)	2.3 (0.05)	2.5 (0.05)
Irvingia gabonensis	16.83 (0.82)	7.97 (0.51)	70.5 (1.92)	2.4(0.08)	2.3 (0.08)

*Values represent mean of three replicates with standard deviation in parenthesis

4.2 Physical properties

Table 4 shows the results of the physical properties of the extracted *Irvingia* extracts. These properties have a major effect on the adhesive performance and determine the penetration and interaction of the adhesive with the substrate. The pH results show that *Irvingia* extracts are mildly acidic with a pH range between 5.09 and 5.76. pH values of most adhesives reported in the literature are in the alkaline region. Dongre et al. (2015) investigated the effect of pH on the mechanical properties of wood adhesive and the three pH conditions tested were in the acidic medium.

The authors stated that at the condition pH below 1, the reaction rate seems to be high enough for crosslinking reactions to take place via lignin-lignin and furfural incorporation. This suggests that base materials in acidic medium enhance adhesive modification.

The specific gravity values range from 0.99 to 1.01. All *Irvingia* extracts obtained had lower pH and specific gravity compared to those reported from other sources such as wheat protein, lupin flour, soy protein and lignin-based.

Table 4: Physical properties of *Irvingia* extract

Samples	Extraction method	pH	Specific gravity
I.wombolu	NaCl	5.1 (27.0°C)	0.99
I.gabonensis	NaCl	5.5 (25.3°C)	0.98
I.wombolu	Water	5.6 (25.8°C)	0.98
I.gabonensis	Water	5.6 (25.6°C)	0.99
I.wombolu	Metabisulphite	5.8 (25.8°C)	1.01
I.gabonensis	Metabisulphite	5.6 (26.5°C)	1.01

*Values represent mean of three replicates with standard deviation in parenthesis

4.3 Effect of extraction on the extract properties

4.3.1 *Irvingia* extract yield

The extract yield varied with species and extraction methods as presented in Figure 12. For *I.wombolu* species, meta extraction gave the highest yield and water extraction resulted in the lowest yield, but for *I.gabonensis* species, NaCl extraction produced the highest yield while Meta extraction gave the least. The post hoc test analysis showed that there was no significant difference ($p > 0.05$) in the effect of species and extraction methods on the adhesive yield, except sample IWM which was significantly different from other samples. The reason could be because of its highest percentage of carbohydrate content.

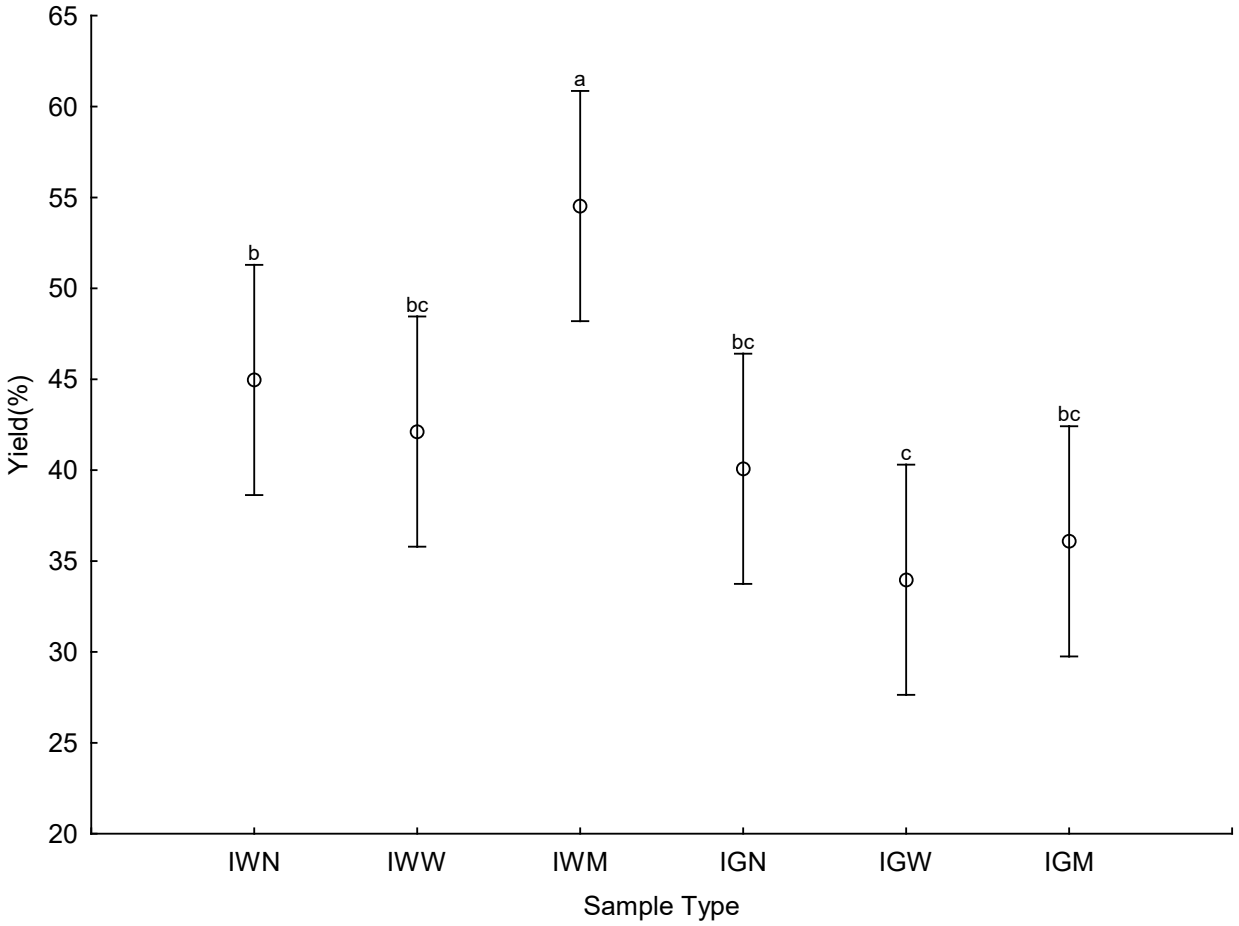


Figure 14: Extract yield from *Irvingia* species using different extraction methods

4.3.2 Composition of *Irvingia wombolu* and *Irvingia gabonensis* extract

The results of the chemical characteristics of *Irvingia* extract are presented in Table 5. The ash content of the extract produced using NaCl and metabisulphite extraction methods were higher than those produced from water extraction. The extract produced through the metabisulphite extraction method had a lower carbohydrate content. This may be due to shorter extraction time of 12 h. The protein contents of all the extract were in the range between 4.8 and 7.9.

Different products had already been developed from the fat content of the kernel such as biodiesel, cooking oil, cosmetics, seasoning cubes and soap (Ainge and Brown 1998; Bello E.I, Fade-Aluko A.O 2011). The interest of this study is to utilise the leftover after the fat content had been used. Three different extraction methods were employed to see the one with highest value of carbohydrate in the extract because the adhesive was projected to be carbohydrate based. All the extraction methods reduced the fat content with water extraction giving the highest values.

There were big differences between results of the kernel composition (Table 3) and extract composition (Table 5). This may be due to the reduction of fat content, which proportionally increased the percentage of the carbohydrate and ash content.

The content of ash was increased substantially following the NaCl and metabisulphite extraction methods. This may be due to the deposit of inorganic elements which were present in their composition. The differences in the carbohydrate content showed the efficiency of different extraction methods.

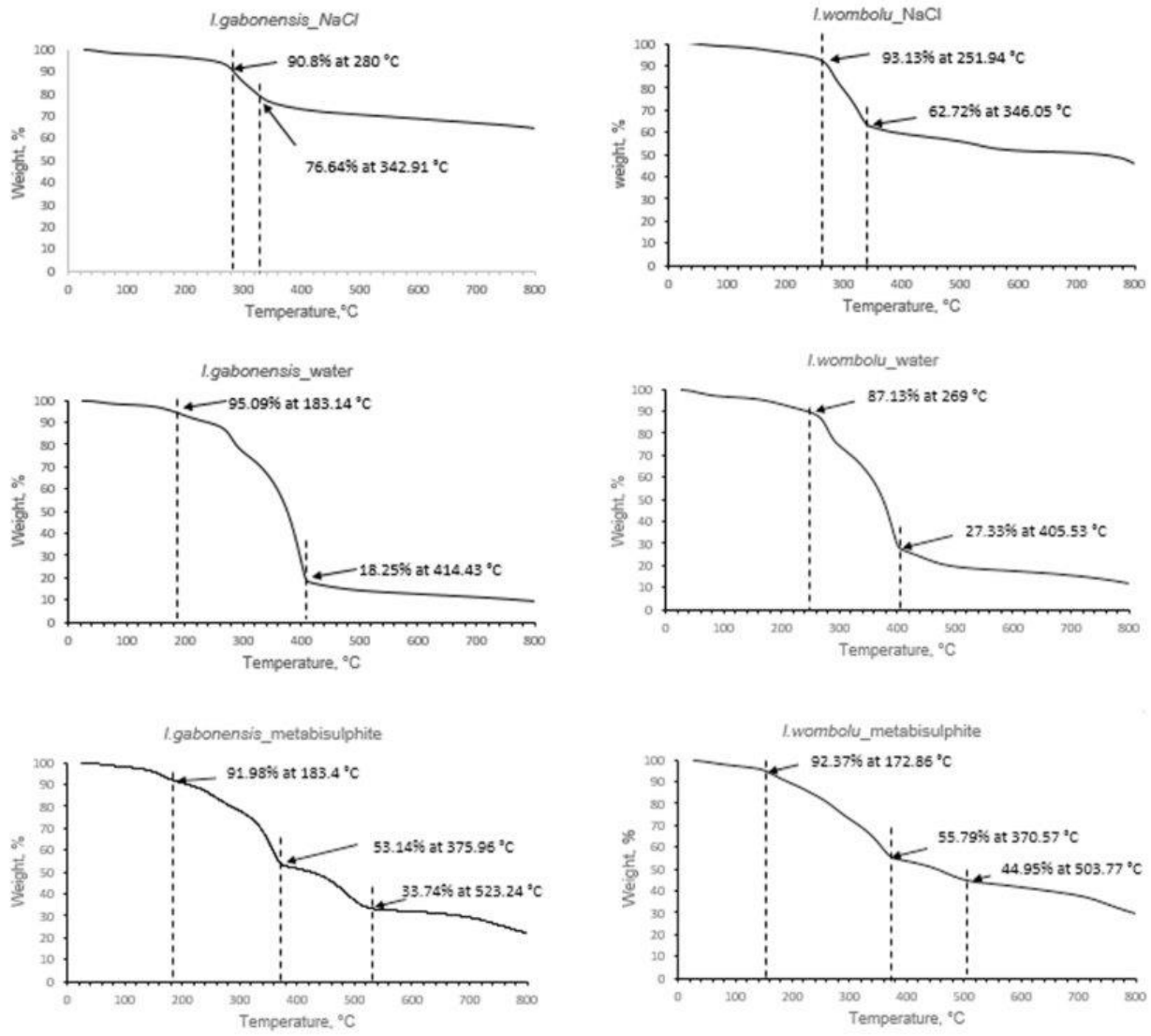
Table 5: Chemical characterisation of *Irvingia* extract

Samples	Extraction method	Carbohydrate (%)	Protein (%)	Fat (%)	Ash (%)	Moisture content (%)
I.wombolu	NaCl	23.8(0.47)	6.95(0.16)	17.5 (2.4)	47.8 (0.57)	4.2 (0.15)
I.gabonensis	NaCl	18.0(0.15)	5.78(0.11)	20.2 (2.4)	52.4 (0.46)	3.6 (0.06)
I.wombolu	Water	43.5(0.16)	4.77(0.28)	40.2 (5.6)	6.1 (0.12)	5.4 (0.25)
I.gabonensis	Water	39.8(0.31)	7.92(0.76)	41.5 (0.7)	6.6 (0.16)	4.1 (0.25)
I.wombolu	Metabisulphite	17.1(0.46)	5.30(0.75)	34.8 (3.0)	31.4 (0.12)	11.4 (0.38)
I.gabonensis	Metabisulphite	13.1(0.13)	5.11(0.14)	36.7 (2.8)	33.7 (0.67)	11.4 (0.17)

*Values represent mean of three replicates with standard deviation in parenthesis

4.4 Thermogravimetric Analysis (TGA)

TGA was used to determine the thermal decomposition and thermal stability of the extract. It is important to understand the thermal properties of the *Irvingia* extract because they require heat to cure. Figure 15 shows the TGA curves. The TGA curves show that there is a minor decrease in weight for all samples at about 100 °C, which is caused by the evaporation of water and partial volatilisation of volatile materials. The second and third stages occurred due to the dehydration of the carbohydrate and protein polymer chains and a complete decomposition of sample residues, respectively (Norström et al. 2014).



a) NaCl extracted *I.gabonensis*, b) NaCl extracted *I.wombolu*, c) Metabisulphite extracted *I.gabonensis*, d) Metabisulphite extracted *I.wombolu*, e) Water extracted *I.gabonensis*, and f) Water extracted *I.wombolu*

Figure 15: TGA curves of *Irvingia* adhesives

From the TGA curves, it can be concluded that the extraction method has a major effect on the decomposition behaviour of all samples irrespective of species variations. Table 6 shows the degradation parameters of *Irvingia* extract samples. The initial decomposition temperature of all extracts ranges from 138.3 °C–149.11 °C and 129.5 °C–145.3 °C for *I. gabonensis* and *I. wombolu* respectively, therefore, the curing temperature can be set around 150 °C. The TGA curves of *Irvingia* adhesives also revealed that NaCl extracted *Irvingia wombolu* has the highest starting temperature for the second stage of decomposition while water extracted *I.gabonensis* had the highest for the third stage. Furthermore, it can be seen that the metabisulphite extracted *I.wombolu* and *I.gabonensis* experienced weight losses in four stages while others only show

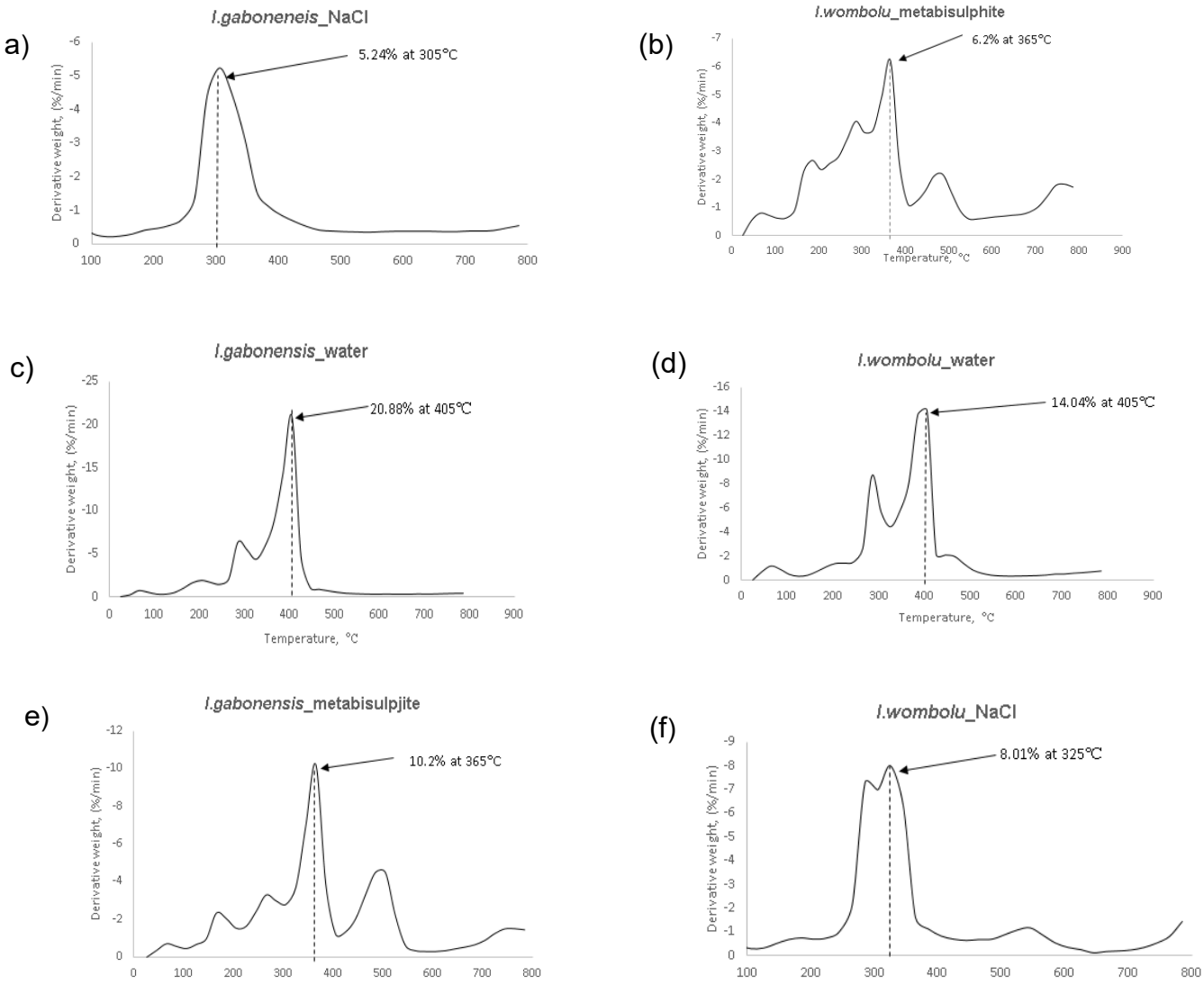
three stages. The reason why the metabisulphite method behaved like this cannot be explained. The highest starting temperatures for weight loss at the second and third stages were found in NaCl extracted *I.wombolu* and water extracted *I.gabonensis,* respectively, while the lowest was found in metabisulphite extracted *I.wombolu*. The residue left after thermal decomposition was the highest with 46% and 65% for both NaCl extracted samples. Water extraction resulted in the lowest residue with 9.6% and 11.7% for *I.gabonensis* and *I.wombolu,* respectively. The NaCl extracted *I.gabonensis* produced thermally more stable extract than the other samples because it gave the least weight loss percentage at the point of maximum decomposition.

Derivative thermogravimetric (DTG curves), as displayed in Figure 16 a-f, are used to determine the maximum rate of decomposition for all samples. According to the DTG curves, NaCl extracted *I.gabonensis* had the least rate of decomposition of 5.24% at 305 °C, while water extracted *I.gabonensis* had the highest rate of decomposition of 20.88% at 405 °C.

Table 6: Degradation parameters of *Irvingia* extract samples

Samples	Inert atmosphere parameters			
	IDT (^{0} C)	$D_{1/2}$ (^{0} C)	MRDT (^{0} C)	Residue (%)
IWN	129.5	719.2	325	46.0
IGN	149.1	-	305	64.5
IWW	145.3	448.7	405	11.7
IGW	142.4	377.0	405	9.6
IWM	132.9	374.36	365	29.8
IGM	138.3	419.95	365	22.3

* IDT = Initial decomposition temperature, $D_{1/2}$ = 50 wt. % decomposition, MRDT = Maximum rate of decomposition temperature.



a) NaCl extracted *I.gabonensis*, b) Metabisulphite extracted *I.wombolu*, c) Water extracted *I.gabonensis*, d) Water extracted *I.wombolu*, e) Metabisulphite extracted *I.gabonensis*, and f) NaCl extracted *I.wombolu*

Figure 16: DTG of *Irvingia* extract samples

4.5 Differential Scanning Calorimetry (DSC)

The DSC thermograms of *Irvingia* adhesives are presented in Figure 17. T_m indicates the melting parameters. The highest melting temperature was found on metabisulphite extracted *I.gabonensis* at 40.92 °C with an energy requirement of 897 J/g (Table 7). The lowest was observed on NaCl extracted *I. wombolu* at 37.27°C with an energy requirement of 121 J/g. The melting temperature of samples of the same species are in a close range irrespective of the extraction method.

According to Table 4.5, *Irvingia* Kernel extract produced through water extraction required the highest energy, while adhesives produced using NaCl required least energy. *Irvingia* adhesives were found to have a lower melting temperature compared to other wood adhesives, for example adhesives produced from oil palm trunk starch, which had a melting point of 88.39°C (Norström et al. 2014).

Energy means the amount of energy required in the phase transition of the material from a solid to liquid. This occurs when the internal energy of the sample increases, typically by the application of heat, which increases the sample's temperature to the melting point. The time stated in Table 7 was the time it took the material to change the phase. From the result given it showed all the samples melted around room temperature. This implication of this is that they can all be modified at room temperature.

Table 7: Parameters of endothermic phase of *Irvingia* kernel extract

Samples	Extraction method	Melting temperature (°C)	Energy (J/g)	Time (min)
I.wombolu	NaCl	37.51	386.2	5.36
I.gabonensis	NaCl	37.27	120.5	5.99
I.wombolu	Water	38.70	1091.7	5.89
I.gabonensis	Water	39.55	835.9	6.10
I.wombolu	Metabisulphite	37.68	651.8	5.92
I.gabonensis	Metabisulphite	40.92	897.3	6.22

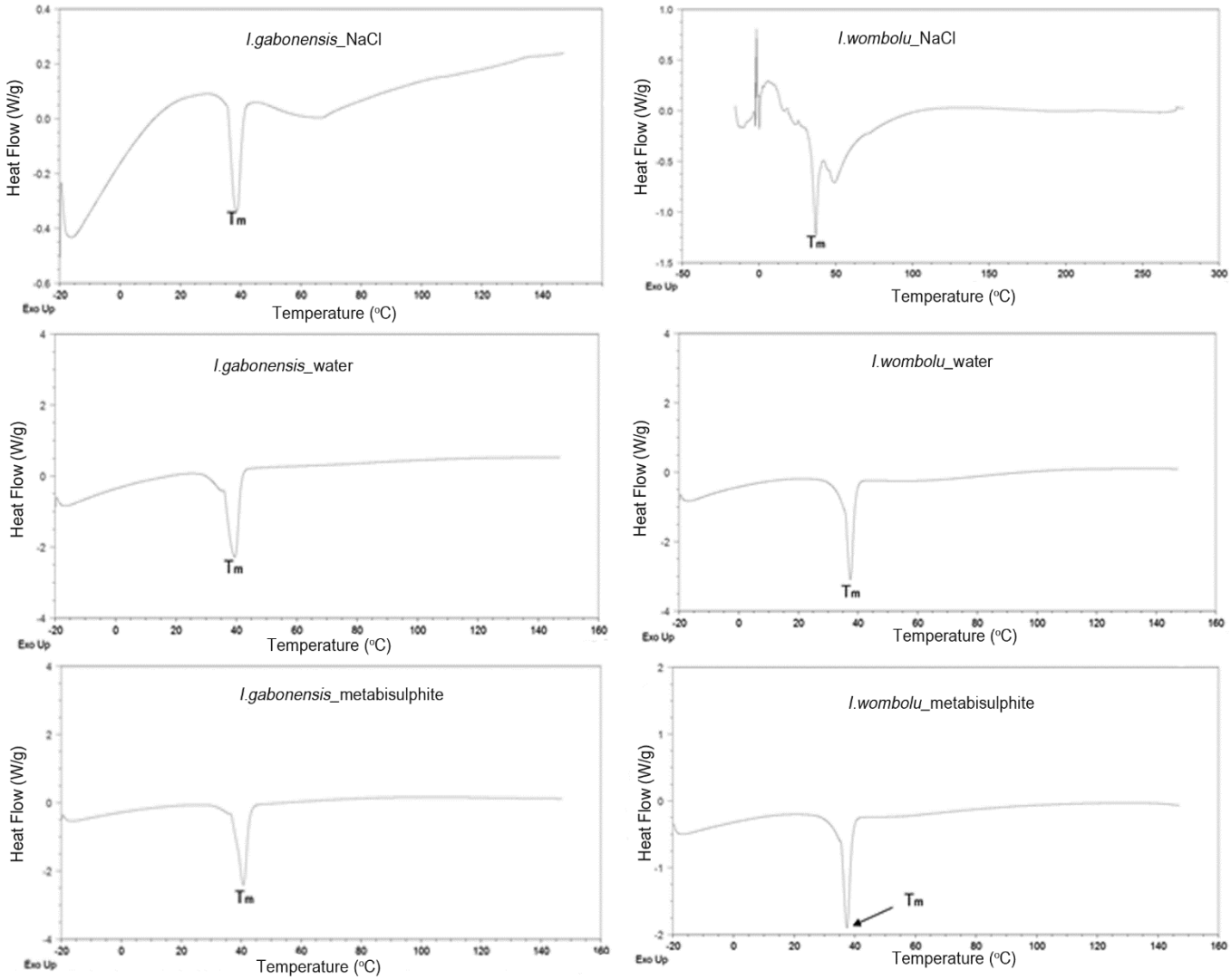


Figure 17: DSC thermograms of *Irvingia* extract samples

4.6 Fourier Transformed Infrared Spectroscopy (FTIR) analysis

FTIR spectroscopy was used to identify functional groups that are present in the extracts. The analysis is useful during modification of the adhesive, as it gives adequate information about its molecular structures. Figure 21 shows FTIR spectra for all samples. The wave number regions and associated functional groups are presented in Table 8. Spectra of the *Irvingia* adhesives are almost similar irrespective of the extraction methods. *Irvingia* extracts have a tendency of forming several kinds of hydrogen bonds due to the presence of a donor N-H and a C=O acceptor group in their linkages. Hydrogen bonds cause poor water resistance of adhesives, because of the interaction between water and hydroxyl groups. The spectra of the *Irvingia* adhesives indicate that absorption peak areas of the hydroxyl group decreased with the increase in carbohydrate content. The broadness of the O-H stretch band was attributed to the presence of carbohydrate in the adhesive.

Table 8: Assignment of the main bands for the *Irvingia* adhesives and their variation with species and method of extraction

	Peaks (cm-1)	Assignment/ Functional groups	References
1	3278 - 3000	O-H and N-H stretch of Amide II/ Intermolecular bonded OH of carbohydrate	(Zhang et al. 2014)
2	2917 - 2916	C-H Asymmetric stretch/ Methylene	(Santoni Ilaria 2013)
3	2850 -	Aliphatic –CH2 stretching vibration	
4	1740 -	O-Actyl ester	(Santoni Ilaria 2013)
5	1728 -	C=O stretch in –COOH (Carboxyl) groups/ ketone	
6	1652 - 1646	C=O stretching vibration/ Protein amide –band I	(Hamarneh et al. 2010)
7	1548 - 1547	C-N stretching of amides/ Amides groups	(Santoni Ilaria 2013)
8	1464 - 1464	C-H bending stretching of methyl and methylene groups	(Naron et al. 2017)
9	1417 - 1413	C-N stretch/ Primary amide	
10	1393 - 1387	C-H stretching in –CH2- and –CH3	(Tiwari and Hihara 2009)
11	1298 - 1270	Ether group	
12	1238 - 1237	C-O groups	(Zhang et al. 2014)
13	1216 - 1204	Guaiacyl structure	(Naron et al. 2017)
14	1173 - 1138	C-O-C groups	
15	1135 - 1102	C-O stretching of aliphatic ether and C-N or NCN stretching of	

		methylene linkages (NCH2N)	
16	1058 - 1043	S=O stretch/ Sulfoxide	(Mostaço-Guidolin and Bachmann 2011)
17	889 - 876	C-H ring vibration/ Pyranoside ring	
18	1000 – 718	The stretching vibration of C-H, C-N and the out-of-plane bending Vibration of N-H could be found at 1000-720 cm^{-1}	(Ibrahim, Nada, and Kamal 2005)

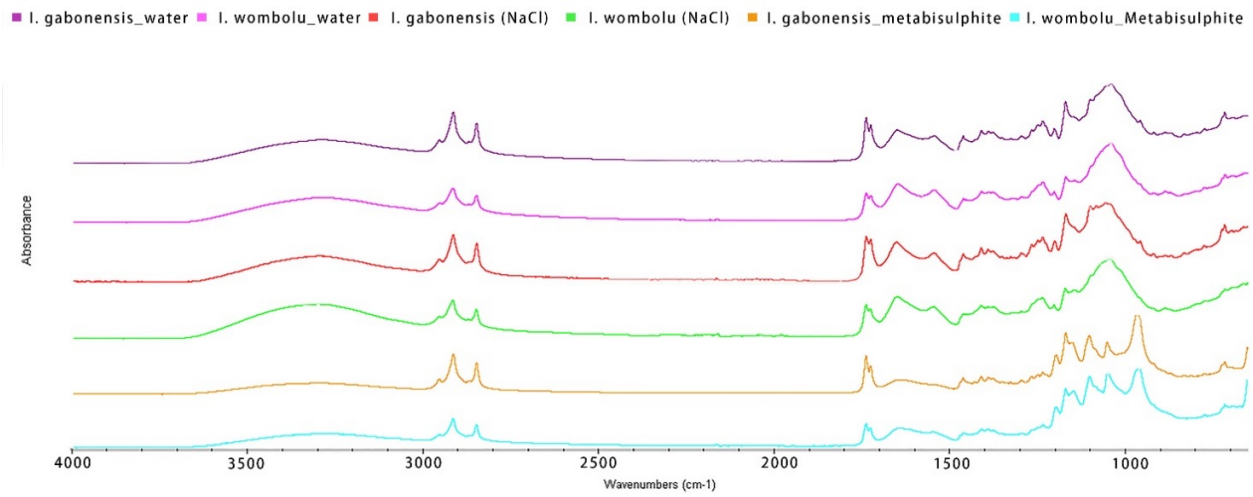


Figure 18: ATR-FTIR spectra of *Irvingia* adhesives

4.6.1 Principal Component Analysis (PCA)

This analysis was used to determine the potential differences within the functional groups among the extract, since they exhibit similar spectra. Principal components PC1 and PC2 explained 91.9% and 7.9% respectively, of the total variability in FTIR spectra data among the extracts. PC1 separates catalytic-enhanced extraction process (positive loadings) from non-catalytic enhanced process. The projection of the PCA results on PC1 and PC2 gave the opportunity to identify three different clusters based on the extraction methods as illustrated in Figure 19. It can be observed that extract produced through water extraction (marked as IWW and IGW) are located at the top negative side of the PC1. This could be partly due to the observed high carbohydrate content in these adhesives.

The extract produced using metabisulphite extraction (marked with IGM) was obviously isolated from other extracts at the bottom section of the negative side of PC1. This could be due to the absence of bands in the wavelength of 1548 and 1297cm^{-1}. This corresponds to the C-N stretching of amides groups and ether groups, respectively, thus contributing to its pronounced separation from other adhesives. The extracts produced using NaCl extraction (marked with IWN and IGN) together with those produced from *Irvingia wombolu* through metabisulphite extraction (marked with IWM) are located on the positive side of PC1, very close to the centre line. This may be attributed to the presence of high ash content in their chemical composition.

On PC2, all samples produced using water and NaCl extraction method had positive or near-zero loadings while adhesives produced from metabisulphite extraction had negative loadings. The presence of the following bands; 1727.48, 1464.07, and 1392.42 cm^{-1} corresponding to C=O stretching in –COOH (carboxyl) groups/ ketone, C-H bending stretching of methyl and

methylene groups, and C-H stretching in $–CH_2$- and $–CH_3$ respectively in IGM caused the variation between IGM and IWM, despite being produced by the same extraction method.

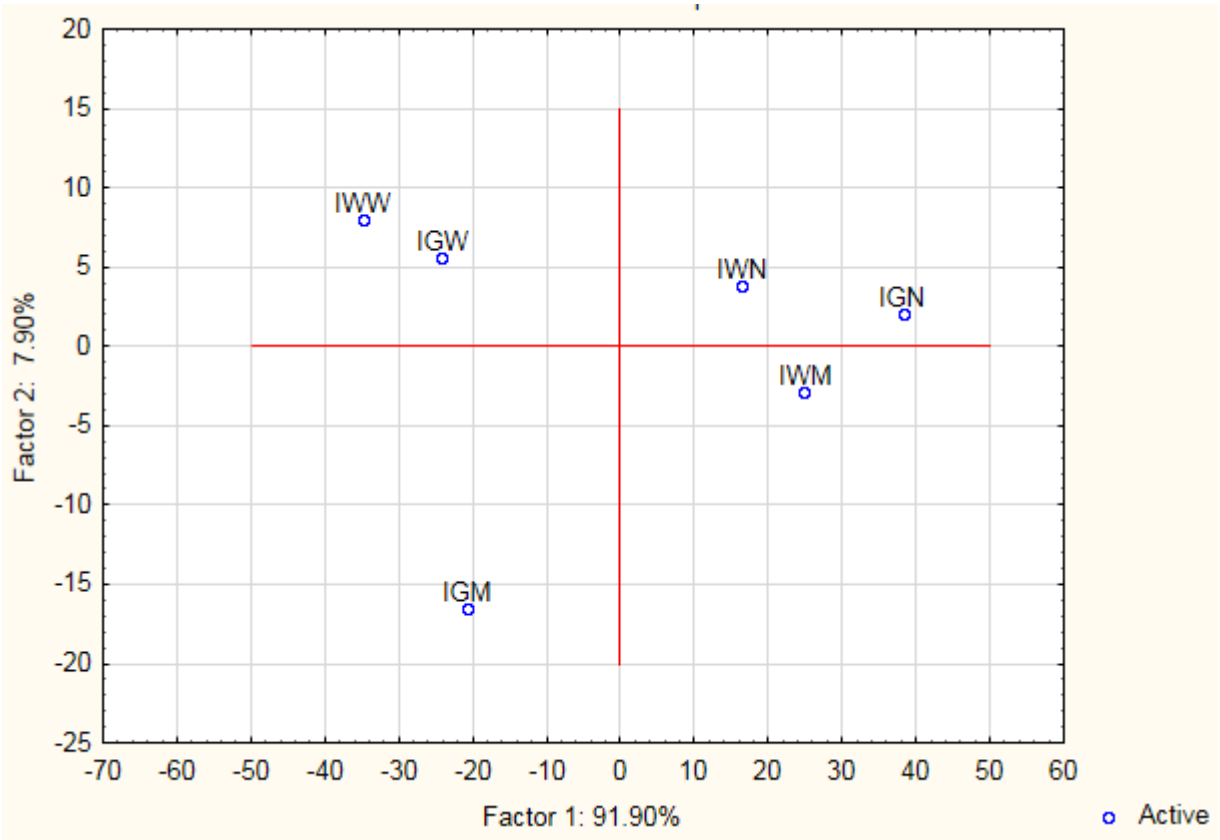


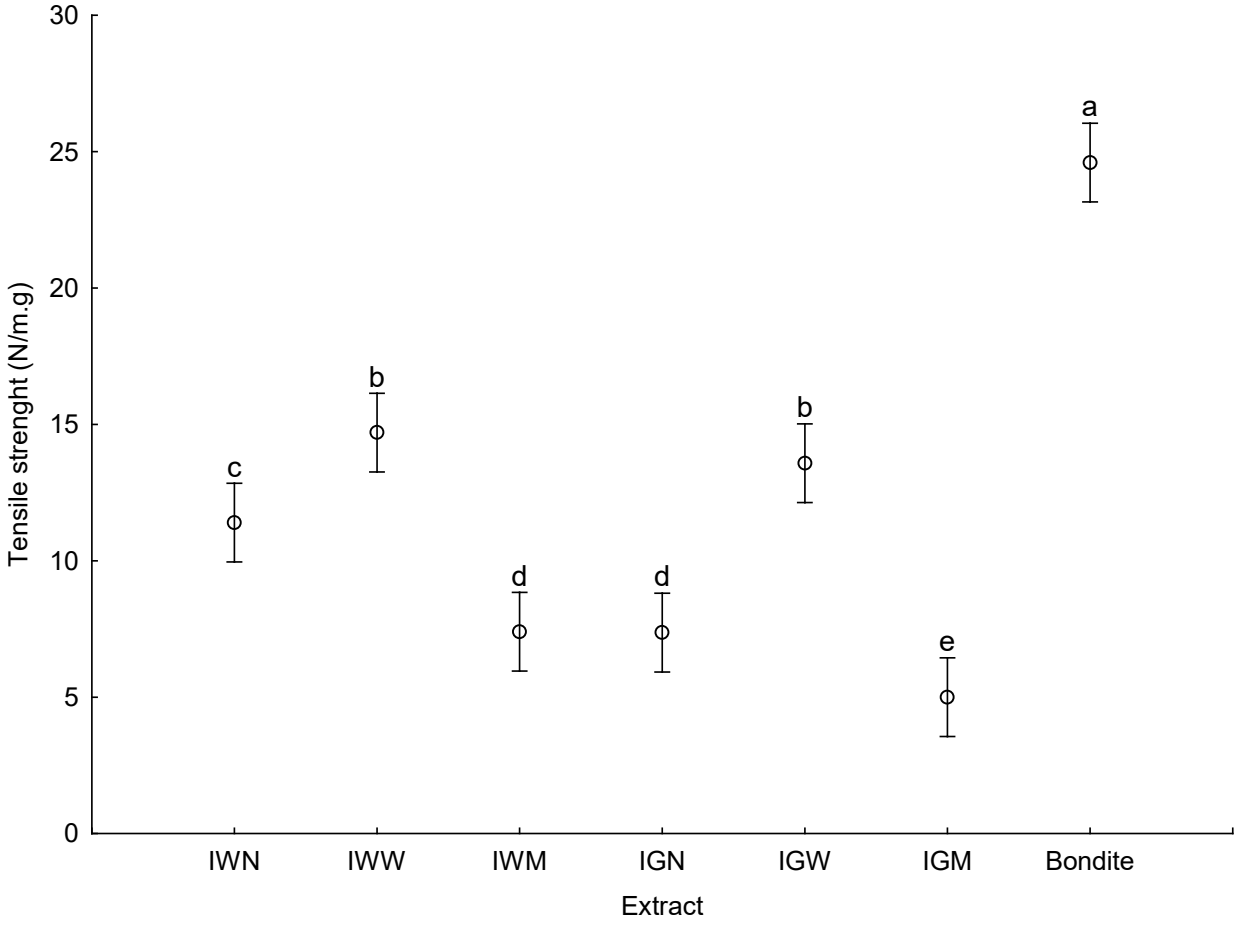
Figure 19: The score plot of PCA model (PC-1 vs PC2) showing variations in FTIR spectra among *Irvingia* adhesives

4.7 Adhesives strength performance

Tensile strength is one of the fundamental properties of polymers and natural fibre-reinforced composites. Tensile strength is the resistance of a material to breaking under tension. The elastic modulus is a measure of elasticity as a ratio of stress to strain produced. These properties are taken here as a measure of the cohesive strength of the various adhesives investigated. However, it has to be noted, that the cohesive strength (property within the adhesive material) is only one factor determining the achievable adhesion strength, with the adhesion behaviour (contact between the adherend and the adhesive) as second factor. The tensile test of the adhesives was conducted using glass fibres impregnated by the adhesives. Figure 20 shows the tensile strength and elastic modulus of the adhesives using the three methods. A comparison was made with the tensile strength of the commercial formaldehyde-based adhesive Bondtite®. Adhesives produced with water extraction had the highest tensile strength and elastic modulus for both species, with values of 46.7 and 44.1 KN/m-g and 14.7 and 13.6 GPa, respectively. This can be attributed to the carbohydrate and ash content in the

samples. It was also observed that the adhesives produced using metabisulphite extraction exhibited the lowest tensile strength and elastic modulus for both species (31.3 and 17.9 KN/m-g, respectively, for the tensile strength; 7.4 and 5.0 GPa, respectively for the elastic modulus). This can also be correlated to the chemical composition, as samples with higher ash and lower carbohydrate contents had lower tensile strength and elastic modulus. The post hoc test results showed significant difference in tensile strength and Young modulus of all samples.

The effect of carbohydrate concentration on the adhesive strength performance was also determined. In all cases, it was discovered that an increased carbohydrate concentration resulted in enhanced strength properties. A high amount of simple sugars indicates better adhesion. This can be observed in the adhesives produced using water extraction process, which exhibited higher strength properties due to their higher carbohydrate quantity compared to adhesives extracted through other processes. This may also be explained by the absence of organic salt in their composition due to the absence of a catalyst. The tensile strength and elastic modulus of Bondtite® was 24.6 N/m-g and 56.7 GPa respectively which were 40.2% and 17.6% higher than the highest tensile strength and elastic modulus respectively, of the extracted adhesives.



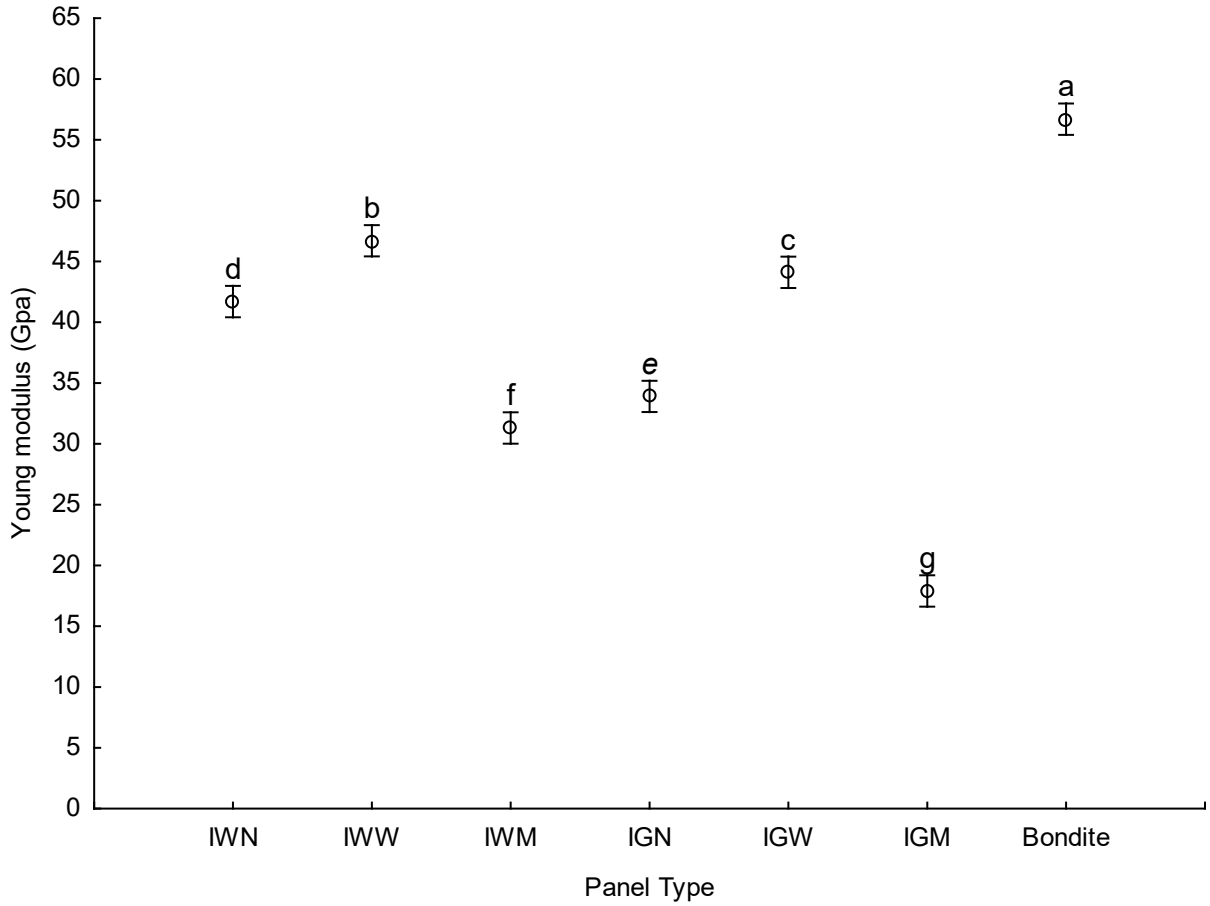


Figure 20: Tensile strength and elastic modulus of the adhesives (p> 0.05)

IWW: water extraction of *Irvingia wombolu*; IGW: water extraction of *Irvingia gabonensis*; IWN: NaCl extraction of *Irvingia wombolu*; IGN: NaCl extraction of *Irvingia gabonensis*; IWM: metabisulphite extraction of *Irvingia wombolu*; IGM: Metabisulphite extraction of *Irvingia gabonensis*

4.8 Final remarks

The FTIR spectra of the Irvingia extracts indicate that absorption peak areas of the hydroxyl group decreased with the increase in carbohydrate content. The TGA results showed the initial decomposition temperature of all extracts ranges from 138.3–149.11 ^{O}C and 129.5–145.3 ^{O}C for IG and IW respectively; therefore, the curing temperature could be set around 150 ^{o}C. It was discovered through DSC analysis that *Irvingia* adhesives have a lower melting temperature compared to other wood adhesives. The strength properties results showed that tensile strength per gram of the kernel extracts ranged from 5.0 to 13.6 KN/m-g and 7.4 to 14.7 KN/m-g for IG and IW, respectively. The moduli of elasticity range from 17.9 to 44.1 GPa and 31.3 to 46.7 GPa for IG and IW, respectively.

The post hoc test analysis showed that there was no significant difference (p> 0.05) in the effect of species and extraction methods on the adhesive yield, except sample IWM which was

significantly different from other samples. The pH results show that Irvingia extract are mildly acidic. The TGA results revealed that extraction methods have a major effect on the decomposition behaviour of all samples irrespective of species variations. Based on the strength comparison with commercially available urea resin Bondtite®, extracts produced using water extraction exhibited comparable properties. The results of the study indicate that *Irvingia* kernel extract is a promising source for non-formaldehyde-based adhesives in wood composite production.

4.9 Conclusions

This study investigated the possibility of developing wood adhesives from *Irvingia gabonensis* and *Irvingia wombolu* kernels extract. The results show that all *Irvingia* extracts are mildly acidic. The chemical characterisation showed that extract produced from water extraction had higher carbohydrate (43.5% and 39.8%), and fat content (40.2% and 41.5%) compared to the extract obtained from other extraction processes. Based on the strength comparison there was significant difference between *Irvingia* extract and commercially available urea resin. In order to improve the strength properties of the adhesives, non-toxic crosslinkers and hardeners are recommended for further study. This is imperative in view of developing alternative formaldehyde-free adhesives for wood-based applications. Therefore, the study concluded that extract developed from *Irvingia* kernel can be used for wood composites manufacturing with the added advantage of environmental sustainability.

Chapter 5: Results and discussion

Evaluation of *Irvingia* modified kernels extract as bio-based wood adhesive

5.1 *Irvingia* adhesives samples description

The kernel extract was used to develop modified adhesives. Water extraction method was used because it produced *Irvingia* extract with best performance on the basis of objective 2 (Chapter 4).

The extract origins and modification methods used to prepare *Irvingia* adhesives samples are indicated by notations in Table 9 below.

Table 9: Extract origins, modification methods and abbreviations of the samples

Extract origins	Modification methods	Notation
I.wombolu	Unmodified	IWN
I.gabonensis	Unmodified	IGN
I.wombolu	Acid/base modified	IWC
I.gabonensis	Acid/base modified	IGC
I.wombolu	Epichlorohydrin modified	IWE
I.gabonensis	Epichlorohydrin modified	IGE
I.wombolu	Glutaraldehyde modified	IWG
I.gabonensis	Glutaraldehyde modified	IGG
I.wombolu	Glyoxal modified	IWLY
I.gabonensis	Glyoxal modified	IGLY

5.2 Fourier Transformed Infrared Spectroscopy (FTIR) analysis

FTIR spectra of the modified *Irvingia* adhesives are shown in Figure 21 and Table 10. The successful modification of the *Irvingia*- based wood adhesives proven with the emergence of new peaks as shown in Table 10. The occurrence of carbohydrates structures present in all samples was confirmed with the presence of O-H bands between 3306–3356cm^{-1} (Santoni and Pizzo 2013). The FTIR spectrum of IGC depicts the characteristic absorption bands of CO and aromatic C=O at 2193 and 1558 cm^{-1}, respectively (Elassal et al. 2011). The absence of the carbonyl ester at 1740 cm^{-1} in all modified adhesives, except IWC and IGC, is attributed to partial hydrolysis of their protein content which could cause breaking of the ester linkage (Santoni and Pizzo 2013). The absorption bands at 1444–1445cm^{-1}, 1421–1422cm^{-1} and 865–868cm^{-1}, which correspond to bending vibrations of the C-H bonds of –CH_3, aromatic skeletal vibrations and/or asymmetric deformation vibrations of C-H bonds in methoxyl groups and C-O-SO_3 of D-galactose -4 sulphate are present in both IGC and IWC [26-27].

Previous studies showed that broadness of the O-H stretch was attributed to the presence of starch in the adhesives. Hydrophilic groups, such as carboxyl and hydroxyl groups might decrease the water resistance of the modified samples (Chen et al., 2013). The appearance of new characteristic absorption bands in modified adhesives as evidenced in Table 5.2, which are absent in unmodified adhesives could be explained by the potential interaction between methoxyl functional groups in hexamine and hydroxyl groups in hardeners and starch molecules. This phenomenon might increase the water resistance of the modified samples.

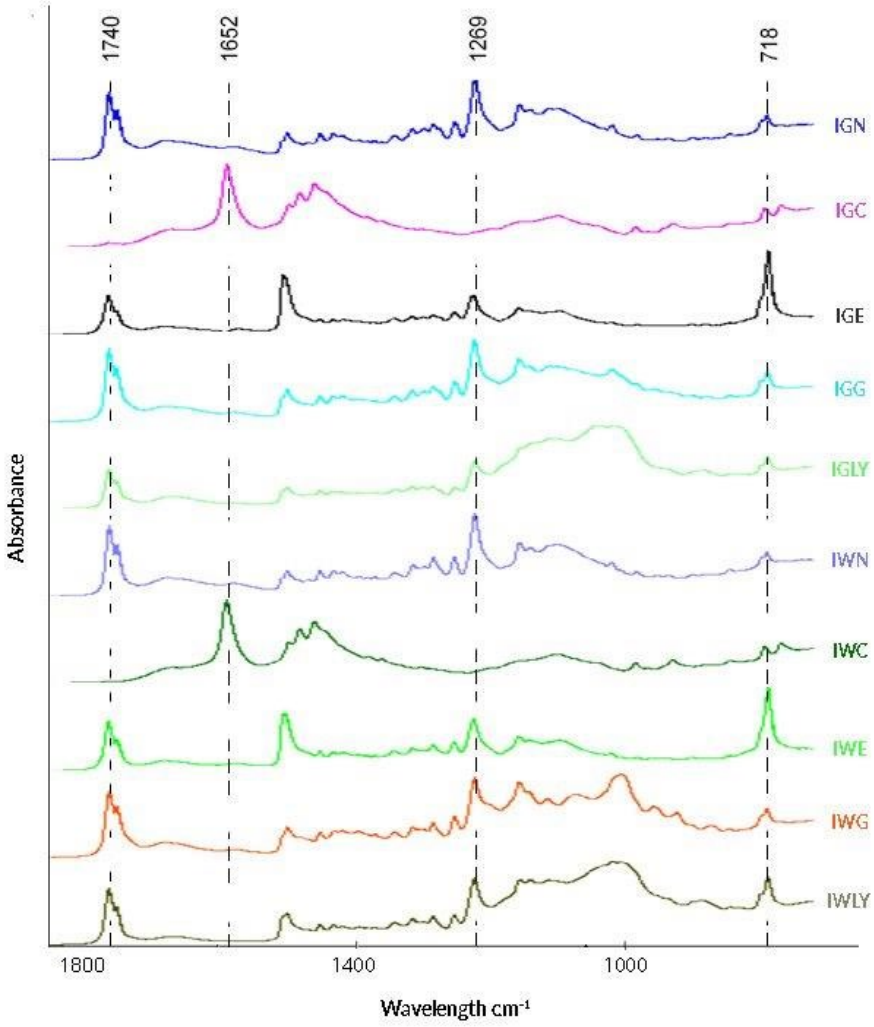


Figure 21: ATR-FTIR spectra of *Irvingia* adhesives

Table 10: Peak, Frequency and Assignment of FTIR Absorption Bands

No	Irvingia-based adhesives samples (cm^{-1})										Assignments/Functional groups	References
	IWG	IWLY	IGE	IGG	IGLY	IGC	IWC	IWE	IWN	IGN		
1	3350	3356	3312	3306	3328	3327	3310	3312	3286	3288	O-H and N-H Stretch of Amide II/ Intermolecular bonded OH of carbohydrate	(Zhang et al., 2014; Zhao et al., 2016)
2	2944	2957	-	2956	2956	-	-	-	2956	2956	C-H	(Zhang et al., 2014)
3	2916	2916	2915	2916	2917	2922	2922	2916	2916	2916	C-H Asymmetric stretch/ Methylene	(Santoni Ilaria, 2013)
4	2850	2849	2849	2850	2850	2848	2849	2849	2850	2850	Aliphatic $-CH_2$ stretching vibration	
5	-	-	-	-	-	2193	-	-	-	-	CO	(Elassal et al., 2011)
6	-	2162	-	-	-	-	-	-	-	-	CH_2CO	(Khachatryan & Pola, 1997)
7	-	1980	-	-	-	-	-	-	-	-	-CO	(Chen et al., 1996; Kappers, Miller, & Koningsberger, 1996)
8	1740	1741	1741	1740	1740	-	-	1741	1740	1740	O-Actyl ester	(Santoni Ilaria, 2013)
9	1728	1729	-	1728	1729	-	-	1728	1728	1728	C=O stretch in –COOH (Carboxyl) groups/ ketone	
10	1652	-	1654	1652	-	-	-	1653	1652	1652	C=O stretching vibration/ Protein amide –band I	(Hamarneh, Heeres, Broekhuis, & Picchioni, 2010)
11	-	1641	-	-	1640	-	-	-	-	-	C=O	(Wu et al., 2016)
12	-	-	-	-	-	1558	-	-	-	-	Aromatic C=C	
13	1545	-	-	-	-	-	-	-	-	-	COO- asymmetric stretching band	(Santoni Ilaria, 2013)
14	-	-	1471	-	-	-	-	-	-	-	C-H bending stretching of methyl and methylene groups	
15	1464	1464	-	1464	1464	-	1461	1468	1464	1464	C-H bending stretching of methyl and methylene groups	(Naron, Collard, Tyhoda, & Görgens, 2017)
16	-	-	-	-	-	1445	1444	-	-	-	Bending vibration of the C-H bonds of $-CH_3$	
17	-	-	-	-	-	1421	1422	-	-	-	Aromatic skeletal vibrations and / or asymmetric deformation vibration of C-H bonds in methoxyl groups	(Kalami et al., 2017)
18	1413	1413	1413	1413	1413	-	-	1413	1413	1412	C-N stretch/ Primary amide	
19	1392	1393	-	1393	1393	-	-	1392	1392	1392	C-H stretching in –CH2- and –CH3	(Tiwari & Hihara, 2009)
20	1379	1379	1378	1379	-	-	-	-	1379	-	Symmetric COO stretching	
21	1353	-	-	-	-	-	-	-	-	-	Symmetric COO stretching	(Ibrahim, Nada, & Kamal, 2005)
22	1328	1328	-	1329	-	-	-	-	1328	-	C=O stretching of Guaiacyl	(Naron et al., 2017)
23	1298	1298	1299	1298	1297	-	-	1298	1298	1298	Ether group	
24	1269	1269	-	1270	1270	-	-	1269	1269	1269	S=O of Sulphate esters	(Distantina et al., 2013)
25	-	-	-	1252	1253	-	-	-	1251	1251	C-O-C Stretching vibration	
26	1237	1237	1238	1237	1238	-	-	1237	1237	1237	C-O groups	(Zhang et al., 2014)
27	-	1205	1205	1204	1204	-	-	1205	1205	1204	Guaiacyl structure	
28	1173	1174	1175	1173	1173	-	-	1175	1173	1173	C-O-C groups	
29	1104	1103	1104	1104	-	-	-	1104	1103	1104	C-O stretching of aliphatic ether and C-N or NCN stretching of methylene linkages (NCH2N)	
30	-	1086	-	-	-	-	-	-	1087	-	PO_2 symmetric stretching	(Mostaço-Guidolin & Bachmann, 2011)
31	1059	1058	-	1058	-	-	-	-	-	-	S=O stretch/ Sulfoxide	(Distantina et al., 2013)
32	-	-	-	-	1047	1045	1044	1042	1045	1045	C-O, C-C stretching or C-OH bending in Hemicellulose	(Hashim et al., 2011)
33	1019	-	-	-	-	-	-	-	-	-	N/A	
34	-	-	-	-	981	-	-	-	-	-	N/A	
35	-	958	-	959	958	-	-	-	960	960	Si-OH stretching	(Tiwari & Hihara, 2009)
36	945	-	-	-	-	-	-	-	-	-	C-O of 3,-6 anhydrous-D-galactose	(Distantina et al., 2013)
37	-	-	-	-	-	922	924	-	921	-	N/A	
38	894	-	-	-	-	-	-	-	-	-	NH_2 twist + CH_2 twist	(Ibrahim et al., 2005)
39	859	-	-	-	-	865	868	-	-	-	C-O-SO_3 Of D-galactose -4- sulfate	(Distantina et al., 2013)
40	-	-	-	835	-	-	-	-	835	-	Aromatic C-H out of plane bending	(Kalami et al., 2017)
41	-	819	-	-	818	-	-	-	-	-	N/A	
42	807	-	-	-	-	-	-	-	-	-	Mannose absorption peak	(Nejatzadeh-Barandozi & Enferadi, 2012)
43	777	777	-	777	-	-	777-772	-	777	-	CH_2	(Pandiarajan et al., 2004)
44	719	718	717	719	718	722	-	718	719	719	N/A	
45	-	-	-	-	-	697	698	-	-	-	NH_2	(Ibrahim et al., 2005)

5.3 Principal Component Analysis

Principal component analysis (PCA) was used to determine the differences within the fingerprint regions of the FTIR spectra among the adhesives and the results are presented in Figure 25. Principal components PC1 and PC2 explained 85.19% and 9.54% respectively, of the total variability in FTIR spectra among the modified and unmodified adhesives. The projection of the PCA results on PC1 and PC2 identified three different clusters based on species and modifiers. PC1 separated epichlorohydrin modified samples (positive loadings) from the other samples. The adhesives modified with epichlorohydrin (IGE and IWE) were isolated from other adhesives at the positive side of PC1, very close to the centre line. This may be due to the absence of the absorption band at 1728 cm^{-1}, which is attributed to the C=O stretching vibration of carboxyl groups. The adhesives modified via acid/base modification process (IWC and IGC) are located at the top negative side of the PC1. This could be partly due to the presence of carbonyl ester, located at 1740 cm^{-1} in these adhesives.

On PC2, the adhesives modified with acid/base modification process and unmodified *Irvingia*-based adhesives are located on the positive side of PC2, very close to the centre line. Glyoxal, epichlorohydrin and glutaraldehyde modified samples are located on the negative side of PC2. This may be due to the presence of a peak at 1379 cm^{-1}, which correspond to symmetric COO stretching.

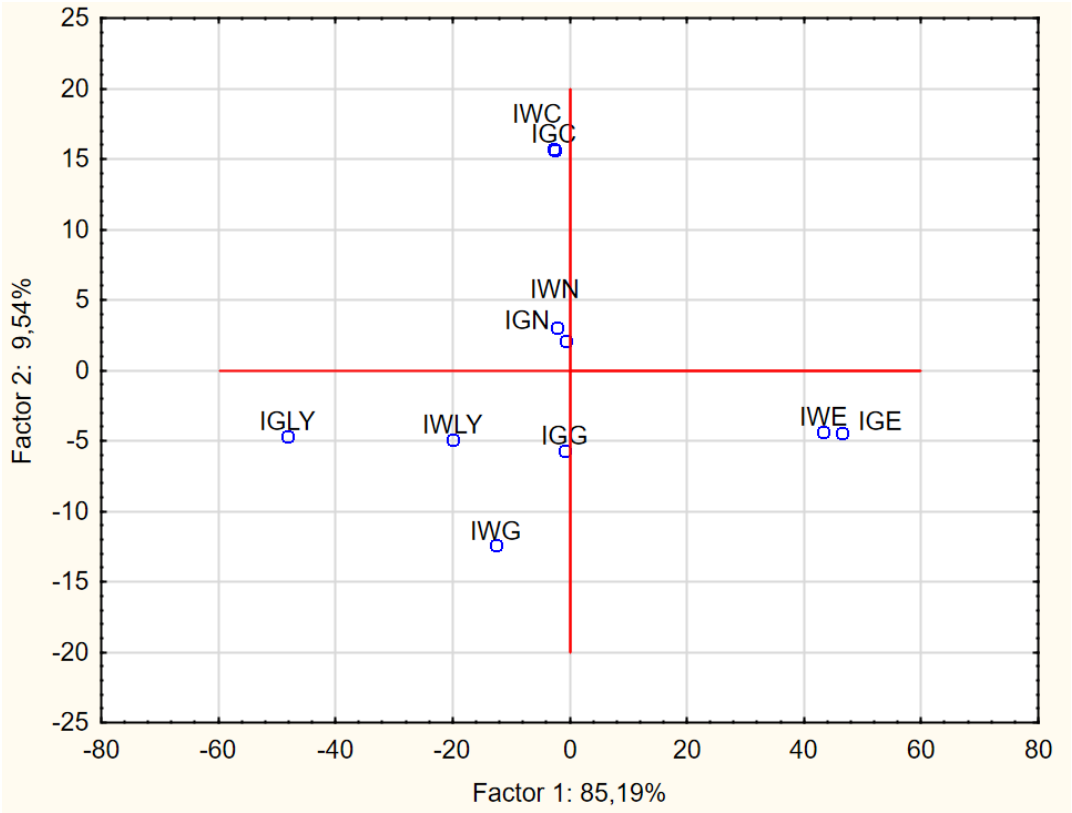


Figure 22: PCA model (PC1 vs PC2) showing variations in FTIR spectra among *Irvingia* adhesives

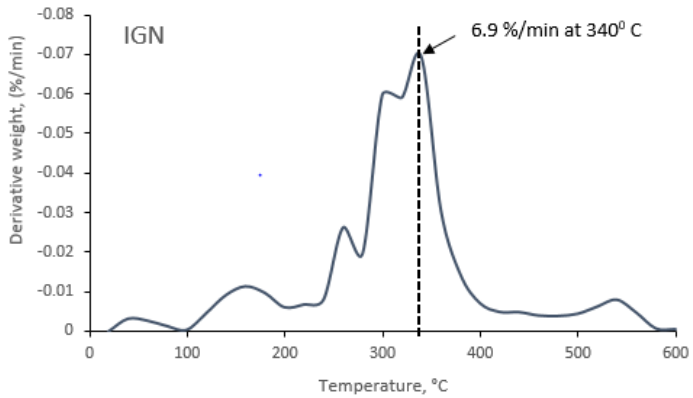
5.4 Thermogravimetric Analysis (TGA)

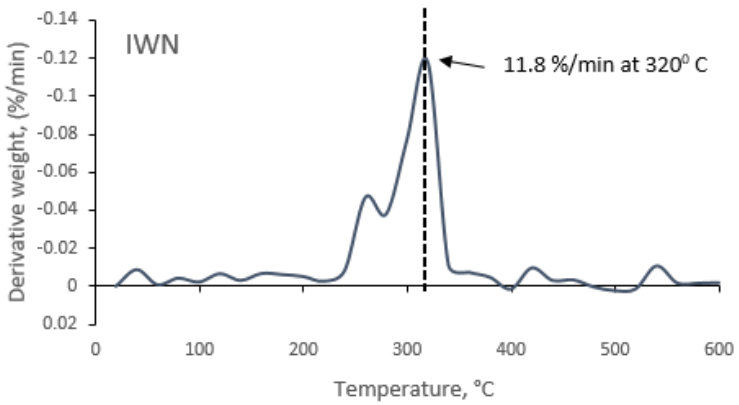
Figure 23 illustrates the thermal stability and decomposition of modified and unmodified *Irvingia* extract samples heated from room temperature to 600 °C. Table 11 lists the degradation parameters. TGA analysis was carried out to measure the percentage of mass loss over the temperature range and the derivative thermogravimetric (DTG) plots show the rate of mass loss through which maximum peak could be used as the degree of thermal decomposition (Kalami et al. 2017). Initial decomposition temperature (IDT) is very important in setting a curing temperature for the adhesives. The peak of DTG_{MAX} may be expressed as maximum decomposition temperature (MRDT) and can be used to compare thermal stability characteristics of different materials (Zhang et al. 2013). The MRDT temperature for all modified samples was between 460 °C and 480 °C, except for the glyoxal-modified samples (IWLY and IGLY). The weight loss in this region was due to dehydration of the polymer chains (Zhang, Ding, Gu, Tan, & Zhu, 2015). The DTG_{MAX} temperature of glyoxal-modified samples was significantly lower than that of the other samples. This is attributed to their crystallinity index as samples with low crystallinity index exhibited low thermal stability (Sulaiman et al. 2013). From Table 11, it can be deduced that the residue left after thermal decomposition was highest for the acid/base modified samples (IWC and IGC) with 44.5% and 41.6%. This revealed incomplete decomposition of their residues and can be related to non-inclusion of hexamine as crosslinking agents in their formulation system.

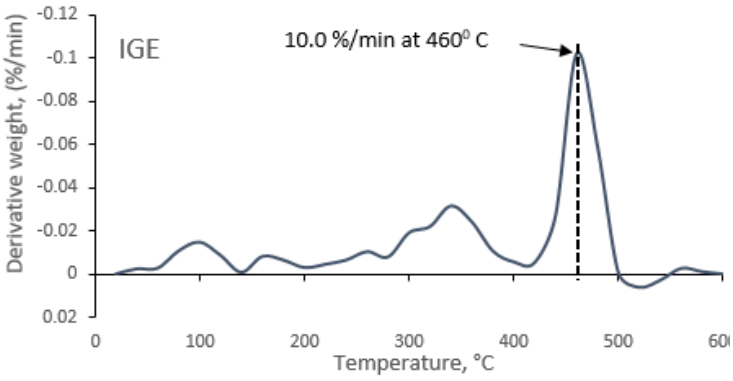
Table 11: Degradation parameters of modified and unmodified *Irvingia* extracts samples

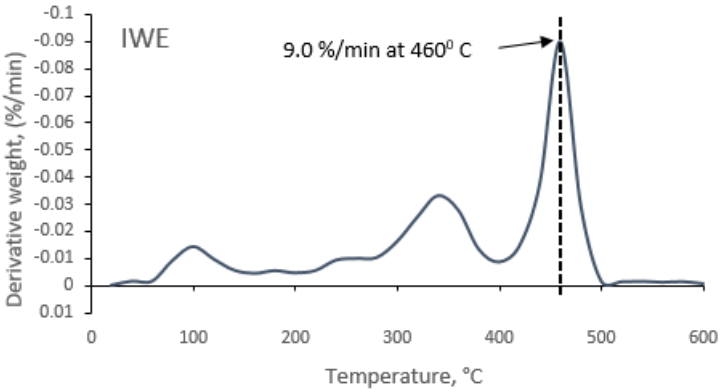
Samples	Inert atmosphere parameters			
	IDT (° C)	$D_{1/2}$ (° C)	MRDT (° C)	Residue (%)
IWN	145.3	306.8	320	7.44
IGN	142.4	320.1	340	3.67
IWC	136.5	469.5	460	44.5
IGC	139.1	472.0	480	41.6
IWE	126.9	385.0	460	4.47
IGE	141.0	436.5	460	4.91
IWG	138.3	422.6	460	0.98
IGG	142.5	402.9	460	5.43
IWLY	132.8	276.1	180	34.6
IGLY	112.8	289.1	160	1.60

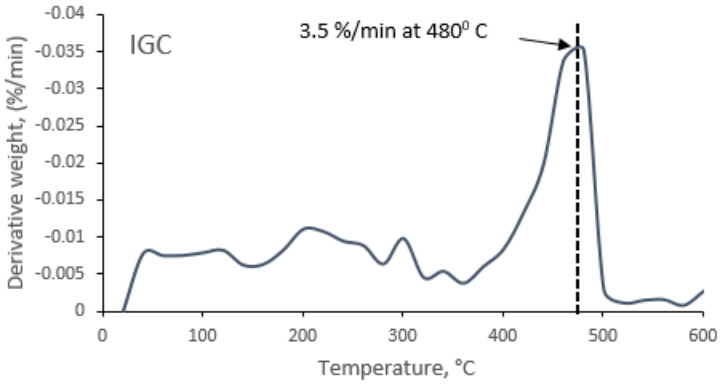
* IDT = Initial decomposition temperature, $D_{1/2}$ = 50 wt. % decomposition, MRDT = Maximum rate of decomposition temp.

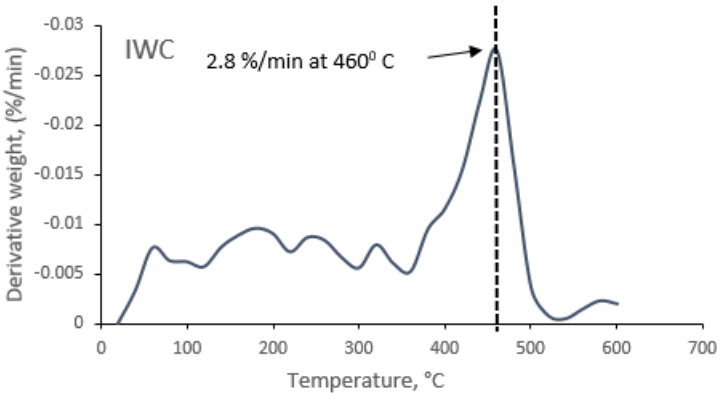












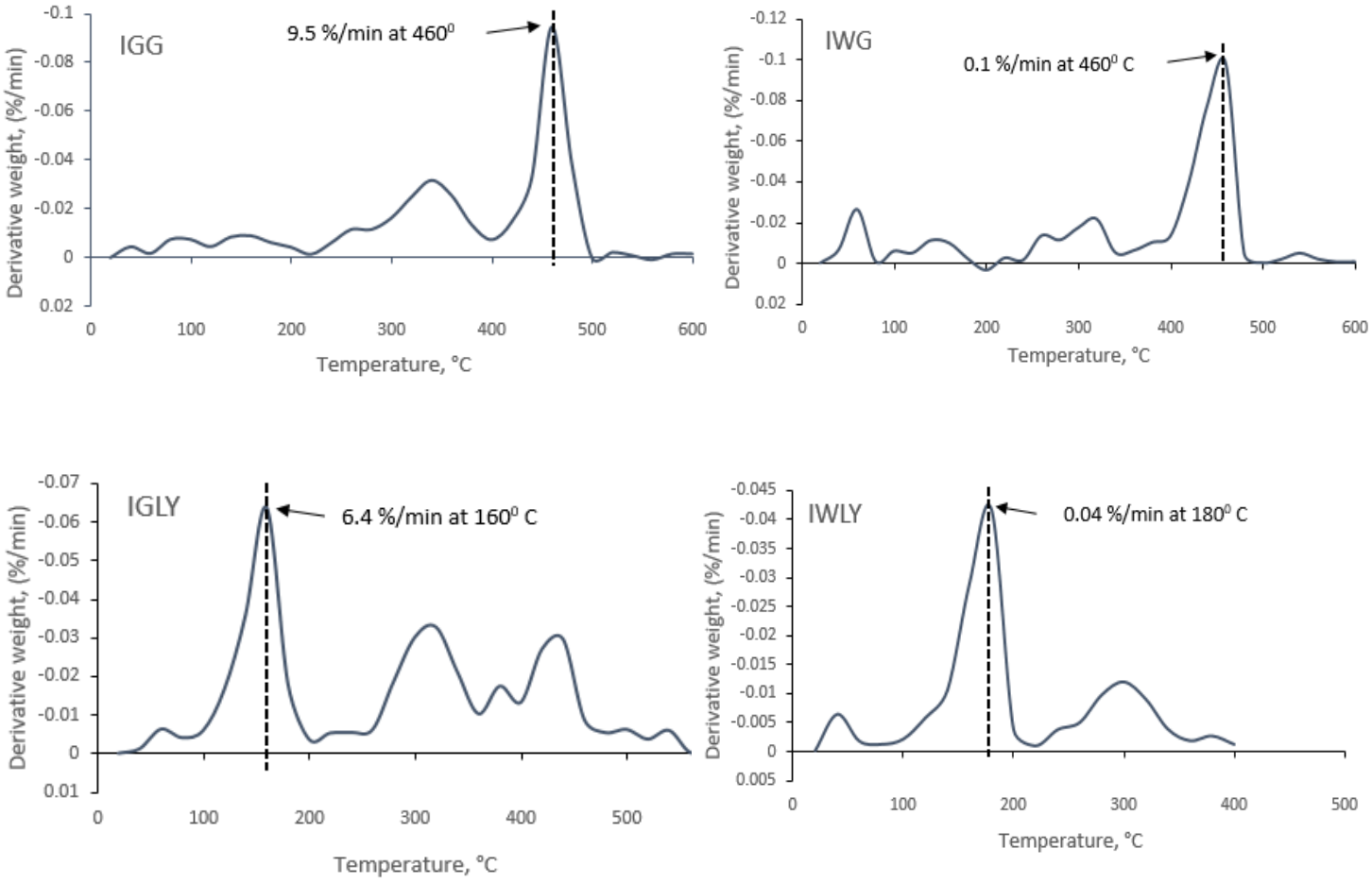


Figure 23: DTG curves of unmodified and modified *Irvingia* adhesives

5.5 Differential Scanning Calorimetry (DSC)

The DSC parameters of modified and unmodified *Irvingia* adhesives are presented in Table 12. The endothermic and exothermic peaks are attributed to melting and curing temperatures of the adhesives respectively (Kalami et al. 2017; Sulaiman et al. 2013). The highest melting temperature was found on glutaraldehyde modified *I.wombolu* (IWG) samples at 125 °C with an energy requirement of 2 071.8 J/g. The lowest was observed on epichlorohydrin modified *I.wombolu* (IWE) samples at 37.3 °C with an energy requirement of 177.6 J/g. From Table 12, it can be seen that the melting temperatures for modified samples are higher than those of the unmodified samples. This observation was in agreement with another research that reported an increase in the melting temperature of modified starch and attributed it to crosslinking reaction that occurs between the starch granules (Sulaiman et al. 2013). The curing temperatures are in a close range, irrespective of species and modification methods between 112 °C and 114 °C and they are lower than curing temperatures of lignin-based adhesives (203 ^{0}C), or commercial phenol resorcinol formaldehyde (PRF) adhesives 195 °C (Kalami et al. 2017). This is an advantage as it implies that minimal temperature will be required to get it cured in the course of

composite production. Modification of all samples clearly shows a reduction in the curing enthalpy compared to the unmodified adhesives. The first exothermic peak can be attributed to an additional reaction between hydroxyl groups in *Irvingia* extracts and methoxyl functional group in the modification crosslinking agent. The second exothermic peak may be caused by the crosslinking of *Irvingia* extracts and crosslinker polymer chains during the curing process (Kalami et al. 2017).

Table 12: DSC parameters of modified and unmodified *Irvingia* adhesives

Samples	Endothermic peak parameters		Exothermic peak parameters	
	Temp (° C)	Energy (J/g)	Temp (° C)	Energy (J/g)
IWN	37.6	214.4	15.4	12,456.4
IGN	41.1	282.6	19.3	10,172.6
IWC	111.6	746.1	-	-
IGC	123.3	704.6	-	-
IWE	37.3	177.6	112.1	3,719.0
IGE	124.6	120.7	112.1	6,539.0
IWG	125.0	2071.8	114.0	9,068.2
IGG	124.0	1450.3	111.2	9,192.9
IWLY	124.7	1159.8	111.3	4,866.3
IGLY	124.6	1559.2	114.0	4,967.0

5.6 Effect of modification on adhesives shear strength

The mean and standard deviations of the shear strength presented in Figure 24 show the force required to separate or de-bond the joined wood pieces glued together (Imman 2001). The adhesive shear strength varies with modification methods and species. The shear strength of unmodified adhesives IGN and IWN are 1.5 MPa and 1.7 MPa, respectively; and these values are about 16% lower for IGN than the shear strength of modified samples with lowest values. Previous analysis has shown that unmodified *Irvingia* adhesives result is about 18% lower in tensile strength and elastic modulus compared to the commercial adhesive Bondtite® (Alawode,

A O, Amiandamhen S O, Meincken M, and Tyhoda L 2018). Glyoxal modified adhesives had the lowest shear strength among modified samples for both species: IGLY had 1.72 MPa and IWLY had 1.74 MPa. Acid/base modified *I.gabonensis* (IGC) had the highest shear strength of 4.05 MPa. This could be due to the reinforcing of *Irvingia* starch granules through crosslinking reaction with hydrogen and sodium hydroxide. The lowest shear strength recorded for modified *Irvingia* adhesives is higher than the minimum requirement for the characteristics shear strength of 1 MPa for panel production for cross layer bond lines according to EN 16352 (2015) standard which is 1 Mpa. This could be attributed to the formation of ether bond during trans etherification reaction which involves interaction between methoxyl functional groups from hexamine and hydroxyl groups in *Irvingia* extract, wood and hardeners (i.e., epichlorohydrin (C_3H_5ClO), glutaraldehyde ($C_5H_8O_2$) and glyoxal ($C_2H_2O_2$). Imam et al. (Imman 2001) reported formation of methanol during trans etherification reaction which leaves the reaction and enters into the solution, thereby giving active bonding properties to the adhesive. This shows that modified *Irvingia* adhesives present good bonding properties. Based on ANOVA analysis on the shear strength of adhesives in relation to different modification methods and species, the analysis showed that only modification methods significantly affected shear strength. There was no significant difference between samples of the same species except glutaraldehyde modified samples. It was observed that there was no significant difference between panels made with unmodified adhesives and glyoxal modified samples.

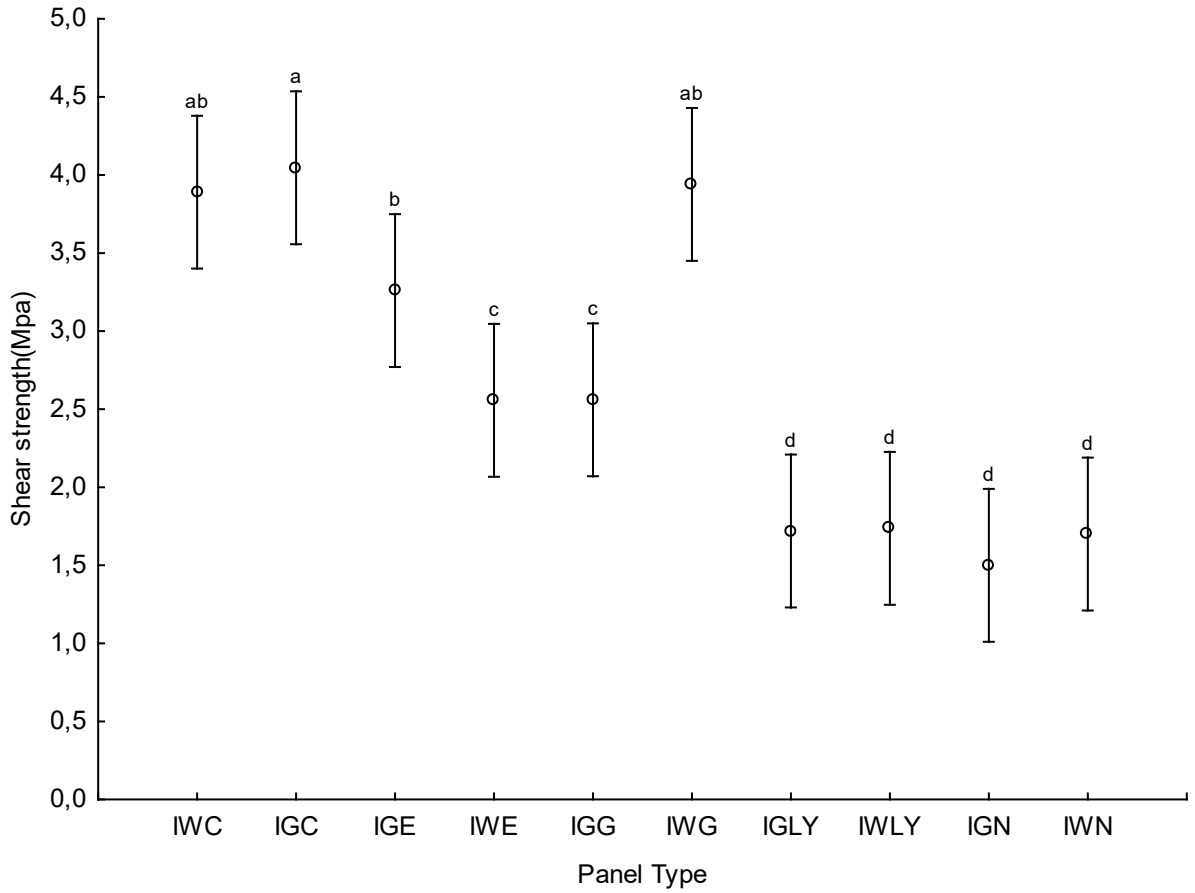


Figure 24: Adhesives shear strength test (p> 0.05)

5.6 Final remarks/discussions

The successful modification of the *Irvingia*-based wood adhesives was proven with the emergence of new peaks in the FTIR results. The derivative thermogravimetric results showed that $(DTG)_{MAX}$ temperature for all modified samples was between 460 °C and 480 °C, except for the glyoxal-modified samples (IWLY and IGLY). The DSC results showed that the curing temperatures of all *Irvingia* adhesives are in a close range, irrespective of species and modification methods between 112 °C and 114 °C. The shear strength of the modified adhesives ranged from 1.72 to 4.05 MPa and 1.74 to 3.89 MPa for IG and IW respectively. The highest values of adhesive shear strength of the modified samples were about 16% higher than panels bonded with IGN (unmodified) adhesives.

5.7 Conclusion

This study examined the feasibility of improving the bond strength of an environmentally friendly natural wood adhesive synthesised from *Irvingia*-based kernel extracts via a modification process using four selected hardeners and hexamine as a crosslinker. TGA and DTG results showed that modified adhesives have low thermal degradation and good thermal stability. DSC

results revealed that the curing temperature of all modified samples is in a close range irrespective of species and modification method. FTIR results showed changes in the functional groups of modified samples, as seen in the emergence of new peaks and bands. The effect of the modification was evaluated through the shear strength of plywood bonded with the adhesives and the results indicated that the shear strength of the modified adhesives was significantly improved except for panels made with glyoxal modified adhesives. Thus, modification of the *Irvingia*-based adhesives resulted in better properties, which contributed to the strength of the adhesives as observed in this study. The main advantage of these modified adhesives is that they do not contain formaldehyde or phenol, both of which are considered potent environmental contaminants.

Chapter 6: Results and discussion

Performance evaluation of a natural based adhesive derived from *Irvingia* kernel extracts on wood panel production

6.1 *Irvingia* adhesives samples description

The modified adhesive produced in Chapter 5 was used to produce wood panel. The adhesives' origins and modification methods used to prepare *Irvingia* adhesives samples are indicated by notations in Table 13.

Table 13: Extract origins, modification methods and abbreviations of the samples

Extract origins	Modification methods	Notation
I.wombolu	Unmodified	IWN
I.gabonensis	Unmodified	IGN
I.wombolu	Acid/base modified	IWC
I.gabonensis	Acid/base modified	IGC
I.wombolu	Epichlorohydrin modified	IWE
I.gabonensis	Epichlorohydrin modified	IGE
I.wombolu	Glutaraldehyde modified	IWG
I.gabonensis	Glutaraldehyde modified	IGG
I.wombolu	Glyoxal modified	IWLY
I.gabonensis	Glyoxal modified	IGLY

6.2 Adhesives crosslinking reaction

According to Imman et al. (2001), ether bond is formed between starch–hexamine; hardeners-hexamine or wood-hexamine during trans etherification reaction which occurs between methoxyl functional groups from hexamine and hydroxyl groups in *Irvingia* extract, wood and hardeners i.e., epichlorohydrin (C_3H_5ClO), glutaraldehyde ($C_5H_8O_2$) and glyoxal ($C_2H_2O_2$). Hexamine is a crosslinking agent with six methoxy methyl groups, which provide an efficient network of crosslinks with the hydroxyl groups in seed extracts, wood and hardeners. During the reaction methanol is formed which leaves the reaction and enters into the solution, thereby giving active bonding properties to the adhesive (Imman et al. 2001). The schematic

representation of the chemical crosslinking reaction of all modifiers is shown in Fig 25. Acid/base modification is not included in the schematic diagram because its formulation system did not contain hexamine as a crosslinker.

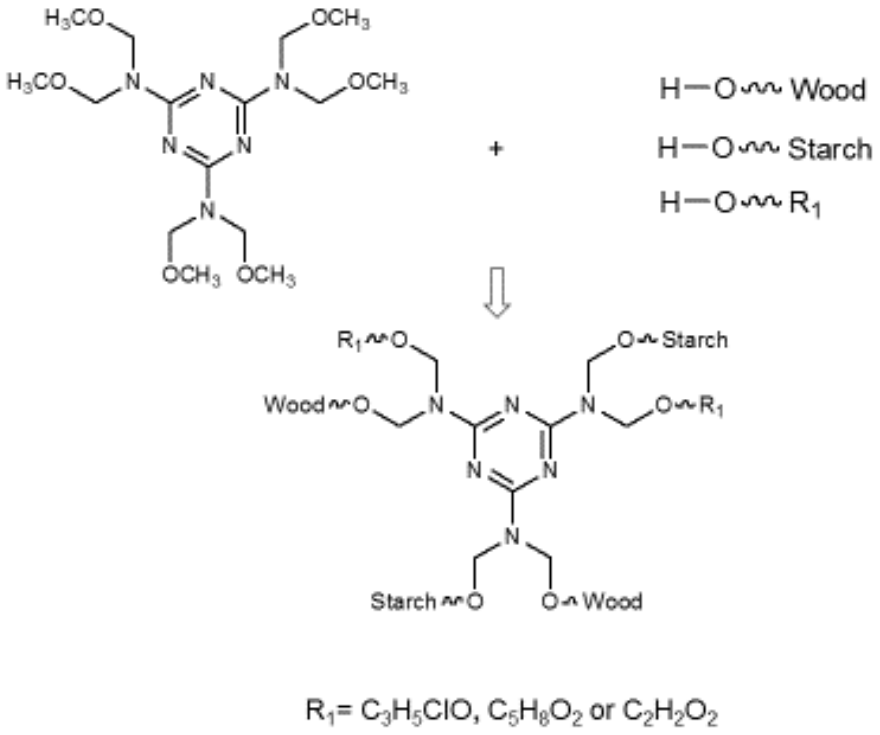


Figure 25: Schematic representation of chemical crosslinking reaction of all modifiers

6.3 Evaluation of functional groups

Fourier transform infrared (FT-IR) spectroscopy was employed to observe any variation between the FT-IR spectra of the manufactured panels produced using different adhesives. The FT-IR spectra of the panels manufactured were quite similar to each other although modifications were clearly different, as shown in Figure 26. FT-IR could not effectively detect variations of the chemical structures related to the different modifications and this may be due to low contents of modifiers. Similar results were reported by Wang et al. (2011) in their study to develop wood adhesives using modified whey protein for manufacturing of structural plywood. Hashim et al. (2011) also reported similar results. The authors state that the functional groups are generally similar for the samples and there was no substantial difference in the peaks of all samples.

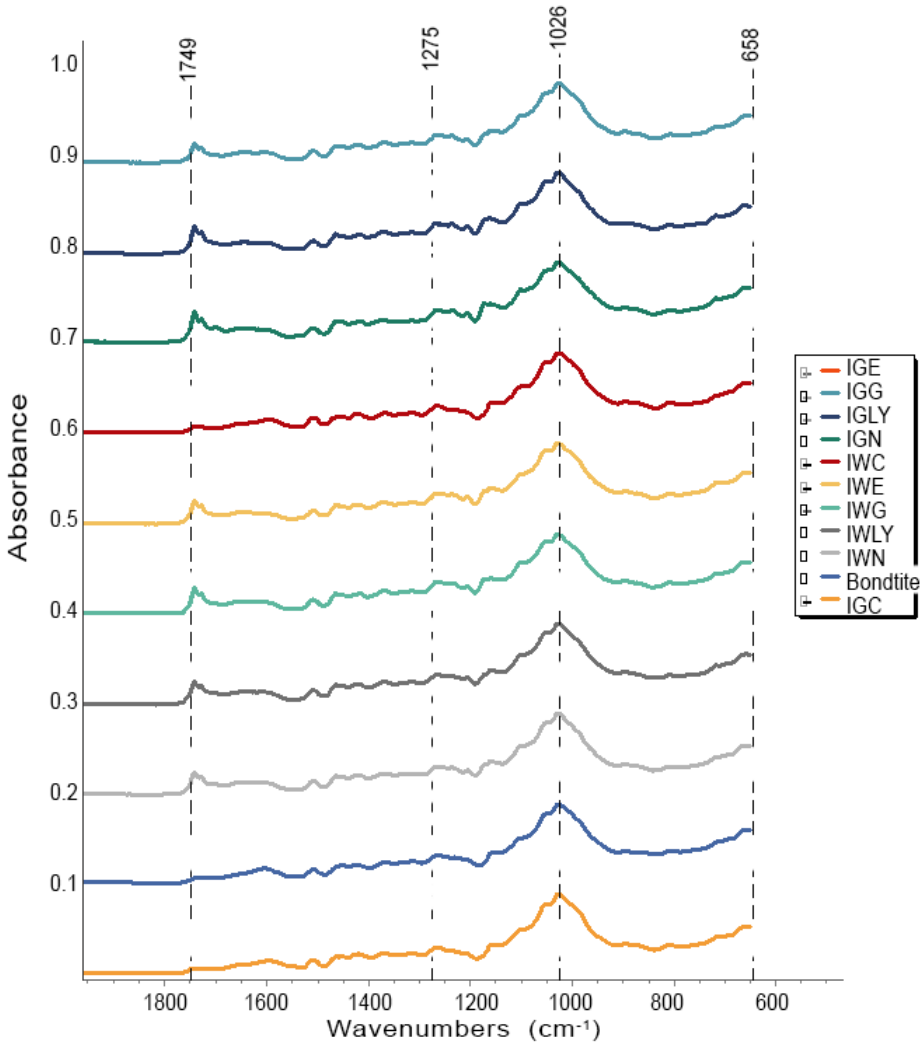


Figure 26: FTIR spectra of panels manufactured using *Irvingia*-based adhesives

6.4 Principal Component Analysis

Principal component analysis (PCA) was further used to determine the potential differences within the fingerprints region of the FTIR spectra among the panels produced with *Irvingia* adhesives and Bondtite® as shown in Figure 27. It is difficult to determine significant variations among the panels with regards to score scatter plots percentage shown. The scores scatter plots PC1 and PC2 explained 99.5% and 0.34% respectively, of the total variability in FT-IR spectra data among panels. The projections on the PCA results on the PC1 and PC2 identified four clusters based on species and modifiers as shown in Figure 30.

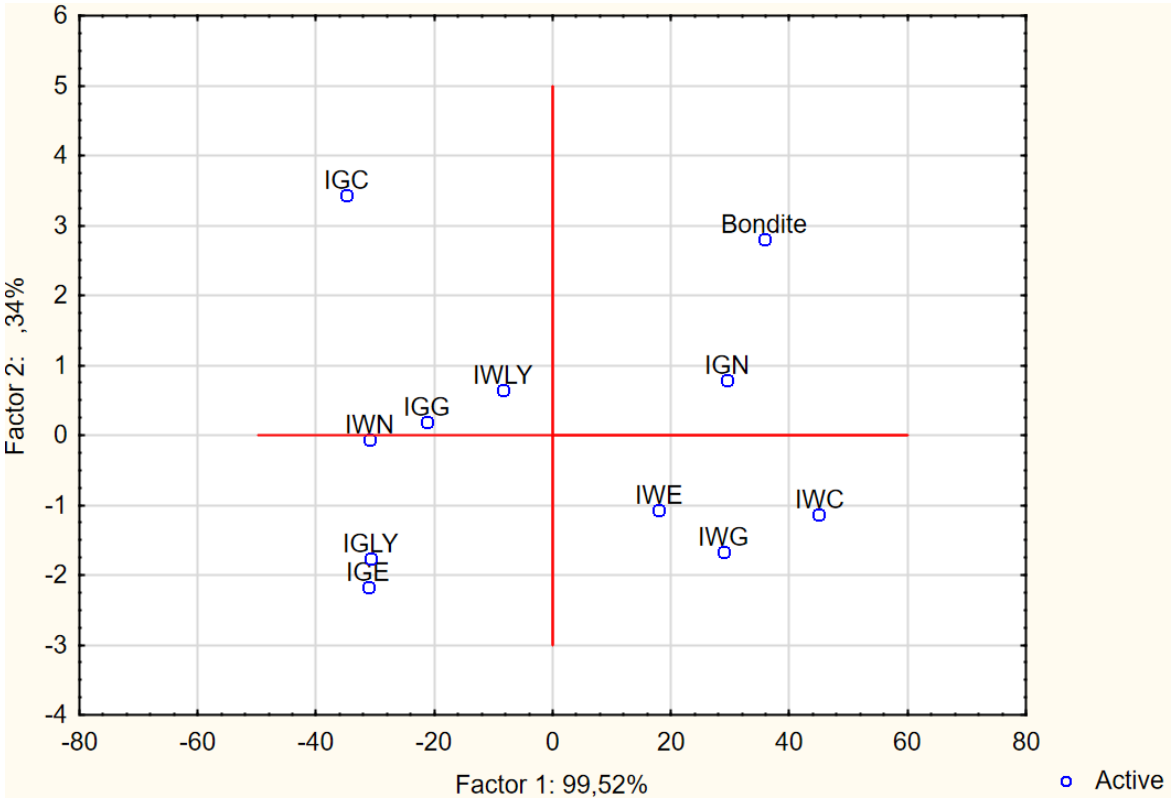


Figure 27: PCA scores plot model (PC-1 vs PC2) showing variations in FTIR spectra among panels

6.5 Physical characterisation

6.5.1 Density

Density is important in material development as it influences other fundamental properties including the strength of the material. According to the American National Standard, ANSI A208.1 (ANSI 2016), particleboards with a density of between 0.60–0.8 g/cm^3 are classified as medium-density panels and above 0.8 g/cm^3 as high-density panels. The mean density of the panels made from a commercial urea-formaldehyde adhesive Bondtite®, unmodified and modified *Irvingia*-based adhesives are presented in Table 14. From the table, the mean density for the different panels was 0.88 g/cm^3, meaning that the boards can be classified as high-density panels except for panels produced with IGC adhesives which can be grouped into the category of medium-density panels. This could be as a result of unanticipated error during its production. For panels manufactured with unmodified adhesives and Bondtite®, the mean densities were in similar range, i.e., 0.9 g/cm^3. For the panels bonded with modified *Irvingia* adhesives, their mean actual density was 0.89 g/cm^3. The actual densities of the panels bonded with modified *Irvingia* adhesives ranged from 0.79–0.94 g/cm^3. The average value of density for panels bonded with native and modified starch from oil palm trunk reported by Sulaiman et al. (2013) was 0.57 g/cm^3. Amini et al. (2013a) investigated the use of modified starch as binder for

the production of particleboard panels made from rubber wood. The author found average actual densities of 0.58, 0.69, and 0.78 g/cm^3 for 0.60, 0.70 and 0.8 g/cm^3 target densities respectively.

Table 14: Density of the panel samples

Panel Type	IWC	IWE	IWG	IWLY	IWN	IGC	IGE	IGG	IGLY	IGN	Bondtite®
Density (g/cm^3)	0.86	0.86	0.93	0.94	0.9	0.79	0.92	0.86	0.91	0.9	0.9

6.5.2 Water Absorption (WA)

The mean and standard deviations of water absorption of boards produced are shown in Figure 28. The WA of the panels ranged from 10 to 21% and 12 to 13% for *I.gabonensis* and *I.wombolu* respectively, except IWC and IGC.

The WA of Bondtite® at 80% was high compared with panels produced with *Irvingia*-based adhesives. This performance is expected of urea formaldehyde bonded panels. The WA for panels produced using unmodified adhesives was 17% for both species, meaning that the binder could be used in environments where the panels could be exposed to water. This could be because *Irvingia* adhesives are starch-based with low content of protein, and the interaction between starch and protein increased gel strength, which thereby increased water resistance. This might be attributed to an increase in the density of protein matrix and the formation of elastic starch globules (Jamilah et al. 2009).

The panels made with IGE and IWE showed the lowest average absorption values for both species. This could be due to formation of highly resistant starch as a result of reaction between an epoxide ring and a chlorine atom within the molecule of epichlorohydrin, and the crosslinker hexamine.

The panel made with IWC did not differ from the panel made with Bondtite® in WA but differed significantly with other panels in this property. The panels produced with IGC adhesives showed the highest WA values. The WA of panels produced with IGC and IWC adhesives were 103%

and 78% respectively. This could be attributed to exclusion of the crosslinker hexamine in their formulation system. The second may be related to lower compaction ratio between particles, resulting in lager empty spaces and therefore better penetration of water in the panel except IGC (Oliveira et al. 2016).

Çetin and Özmen (2003) assessed the properties of particleboard panels produced using a resin developed through partial replacement of phenol with organosolv lignin and found average WA values of 73.2% for LPF20 resin type and 72.9% for LPF30 resin type. Amini et al. (2013b) evaluated the physical and mechanical properties of experimental panels manufactured from rubber wood with modified starch; and observed average WA values of 107.6% for panels of 0.78% measured density.

Nikvash et al. (2013) characterised the physical and mechanical properties of particleboard produced from wheat protein blended with melamine urea formaldehyde and obtained average WA values of 102.3%, 71.7%, and 62.6% for panels of 0.6 g/cm3 density produced with canola, bagasse and hemp wood particles respectively.

The data obtained for most panels bonded with modified adhesives and especially panels made with unmodified adhesives performed better than panels made from urea formaldehyde adhesive Bondtite® and in some cases, lower values were obtained than those reported in the literature for natural adhesives.

Panels made with IWC and IGC exhibited poor moisture resistance. Although panels manufactured with IGE, IWE, IGG, IWG, IGLY, IWLY, IGN and IWN differed in their water absorption values, statistically they are not significantly different.

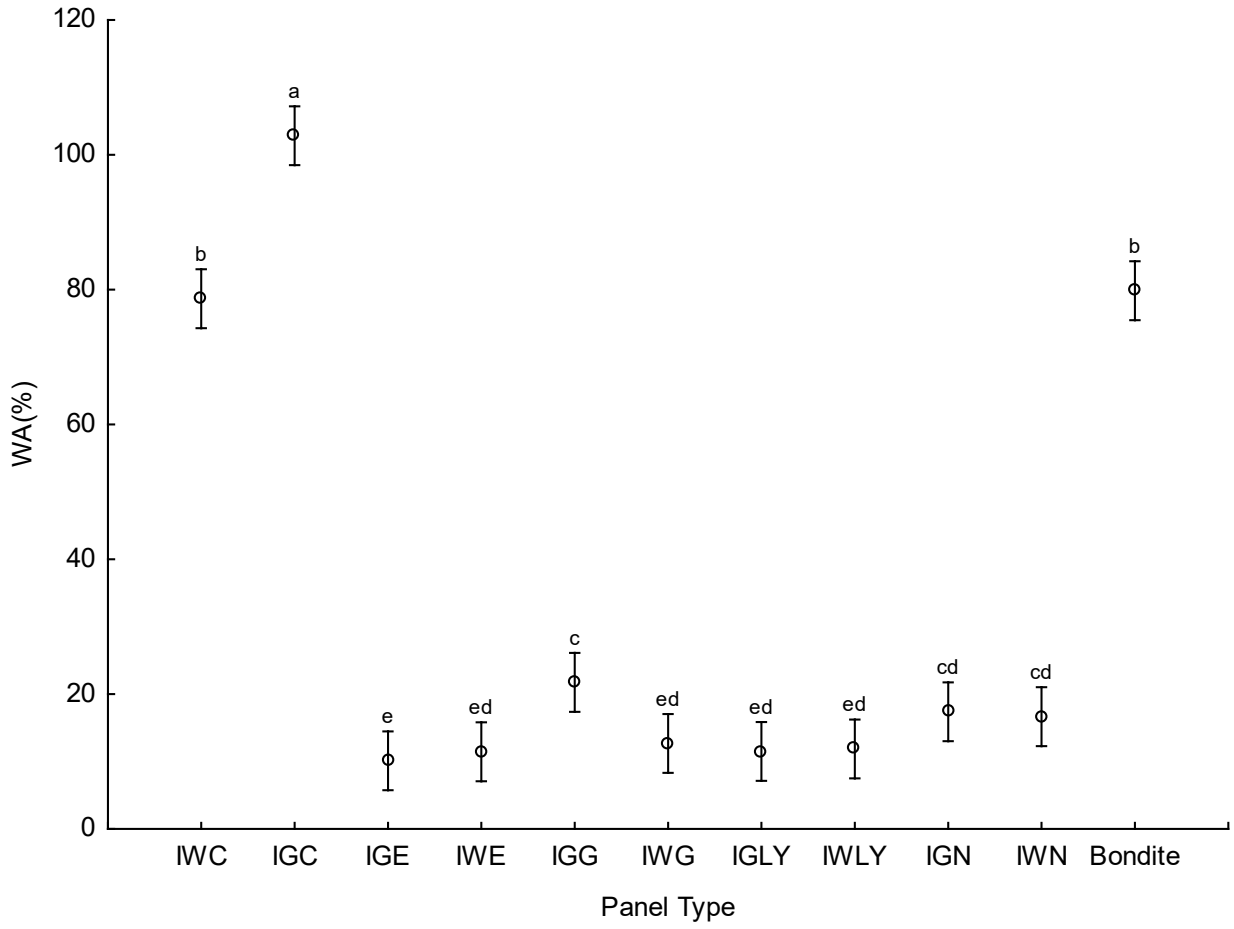


Figure 28: Water absorption of the panel samples (p> 0.05)

6.5.3 Thickness swelling (TS)

The mean values and standard deviations of thickness swelling of boards produced are shown in Figure 29. The TS of the panels ranged from 6 to 17% and 5 to 12% for *I.gabonensis* and *I.wombolu* respectively, except IGC and IWC. All panels made with *Irvingia*-based adhesives met the ANSI A208.1 standard minimum requirement including panels made with unmodified adhesives IGN (10%) and IWN (12%) except for IGC (34%) and IWC (33%). As seen with water absorption, the TS of Bondtite® was also higher (33%) compared with some panels produced with *Irvingia*-based adhesives, which is typical of a urea-based adhesive.

Panels made with IWC and IGC performed worst compared with other panels made with Irvingia adhesives. This unsatisfactory performance may be due to the exclusion of the crosslinker hexamine in their formulation system as well as lower compaction ratio between particles,

resulting in lager empty spaces and therefore better penetration of water in the panel (Oliveira et al. 2016).

Panels produced with IGE, IWE, IGG, IWG, IGLY, IWLY, IGN and IWN actually had different TS values but statistically the differences were insignificant. This trend is similar to what was reported for their water absorption properties performance. This could be because *Irvingia* adhesives are starch/protein based and the interaction between starch and protein with the aid of a crosslinking agent, increased gel strength, thereby increasing water resistance, attributed to the increase in the density of protein matrix and formation of elastic starch globules. The interaction between anionic groups of the starch and the positively charged groups of the protein is mainly electrostatic in nature (Jamilah et al. 2009). For panels with high thickness swelling, several solutions had been proffered, such as treating particles with a water repellent before panel manufacture, the use of heat treatments and surface-coating the end product (Sulaiman et al. 2013). Oliveira et al. (2016) compared industrial panels and found average TS values of 21.1% for pines, 36.5% for eucalyptus and 43.8% for sugarcane bagasse. Cetin and Ozmen (2003) investigated the properties of particleboard panels produced using a resin developed through partial replacement of phenol with organosolv lignin and found average TS values of 12.9% for LPF 20 resin type and 14.7% for LPF30 resin type. Elbadawi et al. (2015) studied the influence of adding a blend of tannins extracted from the bark of two Acacia species on the mechanical and physical properties of particleboard panels made from UF resin and *Ailanthus excelsa* wood raw material. They found higher TS2h and TS24h values as the percentage of tannin extract was increased, with average values ranging from 37.3 to 41.8% for TS2h and from 42.9 to 47.6% for TS24h.

In general, it was observed from the physical properties evaluated, pending ageing studies, that panels produced with modified *Irvingia* adhesives are promising for outdoor applications.

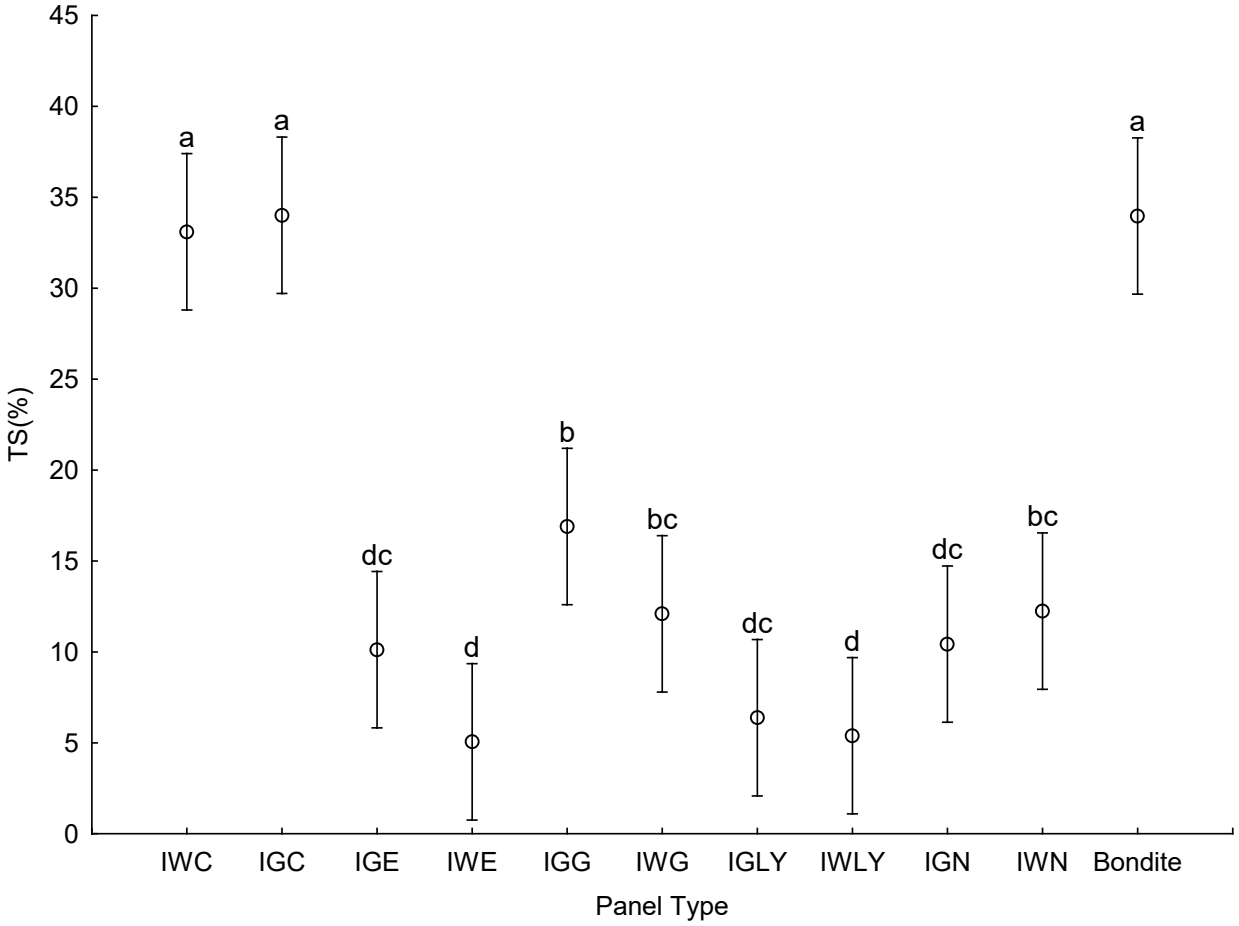


Figure 29: Thickness swelling of the panel samples (p> 0.05)

6.6 Mechanical Characterisation

6.6.1 Modulus of rupture

The flexural properties of samples with different modifications were evaluated through the measurement of the modulus of rupture (MOR) as shown in Fig. 30. The MOR values ranged from 3.3 to 7.4 MPa and 5.4 to 6.9 MPa for *I.gabonensis* and *I.wombolu* respectively. There was no significant difference among panels made with *Irvingia*-based adhesives but differed significantly with panels made with Bondtite®.

The highest MOR was found with panels made with IGE (7.4). This could be due to the reinforcing of *Irvingia* starch granules through crosslinking reaction with epichlorohydrin (Sulaiman et al. 2013). The lowest values for MOR were found for the panels bonded with IGC (3.3 MPa). This may be attributed to exclusion of hexamine in their formulation procedure. The MOR obtained for panels bonded with unmodified adhesives IGN and IWN were 5.2 and 6.7 MPa respectively. The highest MOR values for the species were about 30% and 3% higher than unmodified samples for *I.gabonensis* and *I.wombolu* respectively.

Amini et al. (2013b) assessed particleboard panels of rubberwood spp. produced with modified starch adhesive, with densities of 0.60, 0.70 and 0.80 g/cm^3 and found average MOR values of 9.85, 12.87 and 20.38 N/mm^2 respectively. Sulaiman et al. (2013) determined the properties of particleboard panels produced with oil palm starch modified with epichlorohydrin. The average value of MOR ranged from 7.6 and 19.1 N/mm2 for the 0.80 g/cm^3 density panel bonded with modified starch.

In a nutshell, the average values obtained in this present study for panels made with *Irvingia*-based adhesives and Bondtite® were below some of the values reported in the literature. However, according to the ANSI A208.1 standard, panels bonded with IWG, IWLY, IWN, IGE, IGG and Bondtite® met the minimum requirements standard and are categorised within grade 1-L-1.

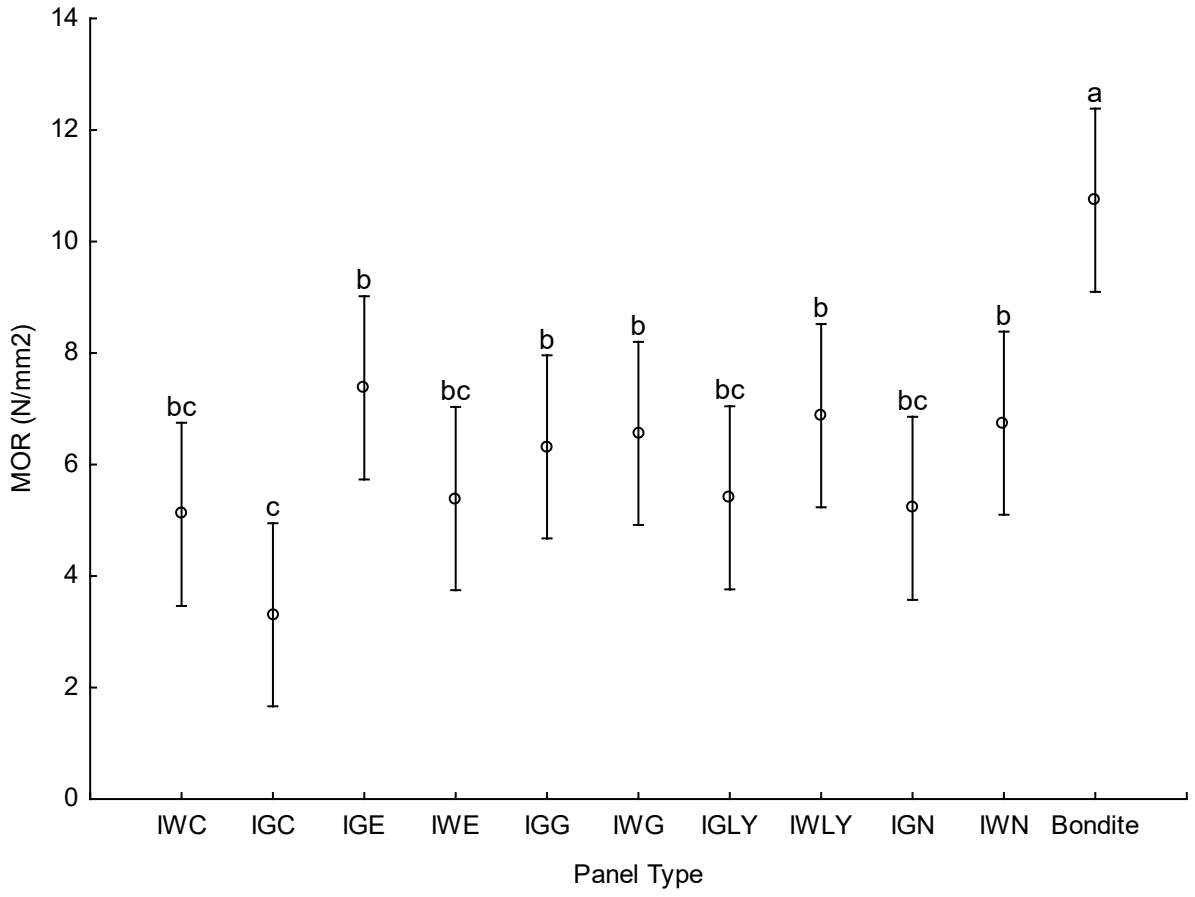


Figure 30: Modulus of rupture of the panel samples (p> 0.05)

6.6.2 Modulus of elasticity

The stiffness properties of samples with different modifications were evaluated by the modulus of elasticity (MOE). The mean and standard deviations of the MOE of the panels are shown in Figure 31. The average values of all treatments did not differ significantly from one another for

all panels, except IWLY and IGC. The difference between IWLY and IGC may be due to their modification and species variation. Comparing panels made with Bondtite® and panels produced with IGE, IWG, IWLY and IWN, the differences were not significant. The mean MOE values of the panels ranged from 458 to 1281 MPa and 660 to 1580 MPa for *I.gabonensis* and *I.wombolu* respectively.

Oliveira et al. (2016) compared industrial panels and found average values of the MOE to compression to be 921.0 MPa for pine, 1224.7 MPa for eucalyptus and 754.1 MPa for sugarcane bagasse. Sulaiman et al. (2013) produced particleboard panels using oil palm starch modified with epichlorohydrin. The average value of MOE ranged from 1695.2 and 3471.6 MPa for the 0.80 g/cm^3 density panel bonded with modified starch.

According to the ANSI A208.1 standard all the panels manufactured with *Irvingia*-based adhesives and Bondtite® met the minimum requirements and can be categorised within grade LD-1, except panels bonded with IWC and IGC adhesives.

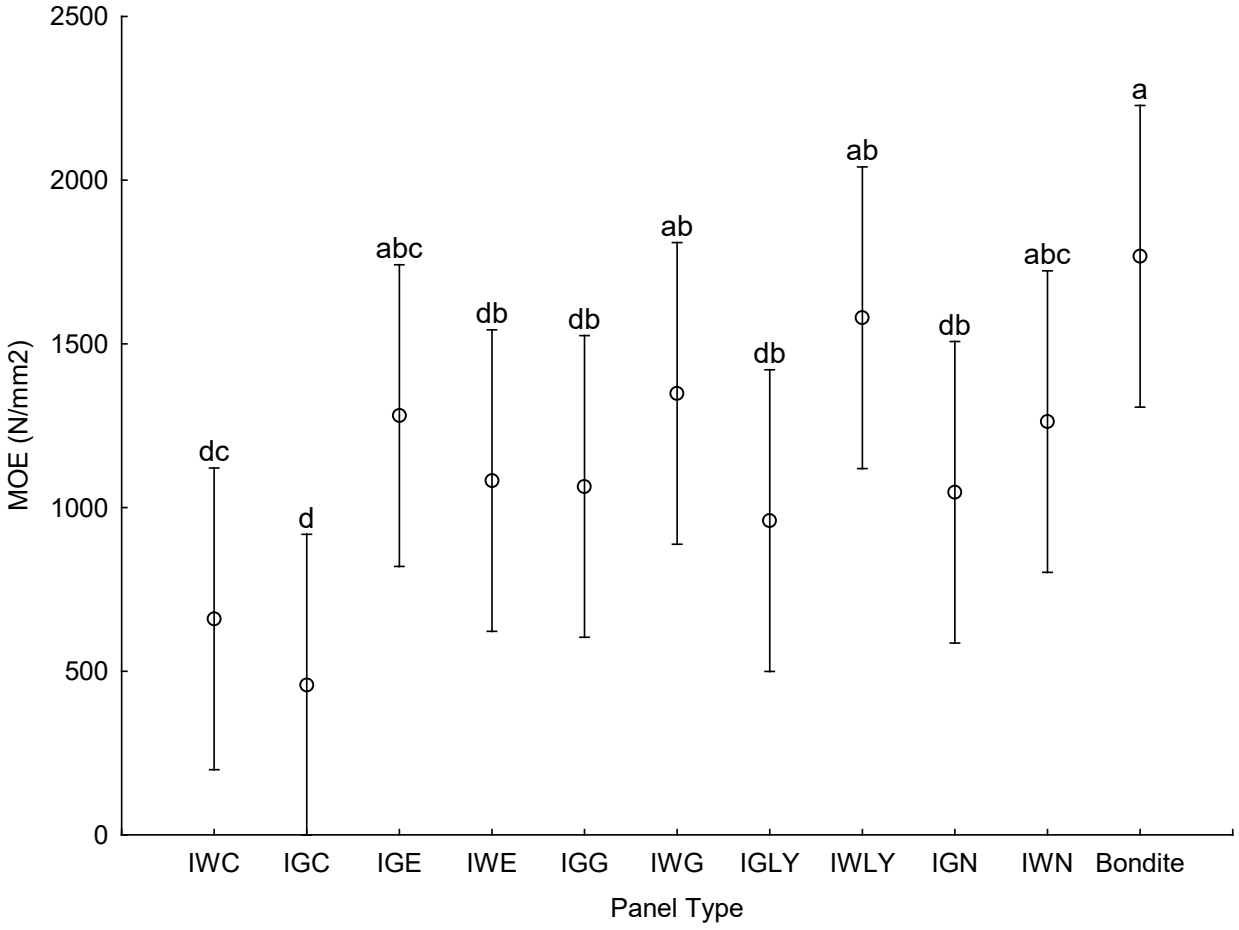


Figure 31: Modulus of elasticity of the panel samples (p> 0.05)

6.6 Final remarks

The modulus of elasticity (MOE) of the panels ranged from 458 to 1281 MPa and 660 to 580 MPa for IG and IW while modulus of rupture (MOR) of the panels ranged from 3.31 to 7.38 MPa and 5.11 to 6.88 MPa for IG and IW respectively. The mean values of MOR and MOE for the panels produced with *Irvingia*-based adhesives were 5.8 and 1251 MPa respectively. The values are within the minimum required MOR and MOE (5.5 and 1034 MPa respectively) for panel grade 1-L-1 as specified in the American National Standard (ANSI A208.1). These panels are recommended to be used as core material for solid doors. FT-IR results could not effectively detect variations of the chemical structures related to the different modifications and this may be due to the low content of modifiers. It was observed from the physical properties evaluated, pending ageing studies, that panels produced with modified *Irvingia* adhesives are promising for outdoor applications because they exhibited good water resistance properties. The flexural results show that all the panels manufactured with *Irvingia*-based adhesives and Bondtite® met the minimum requirements and can be categorised within grade 1-L-1 according to ANSI A208.1 standard, except panels bonded with IWC and IGC adhesives. These panels are recommended to be used as core material for solid doors. Since there were no significant differences between panels made with unmodified adhesives in all properties considered. It can be concluded that modification of the adhesives may be considered not to be necessary, although there was slight improvement in some of the properties. Optimisation of these modifiers and crosslinkers may be considered in a future study in order to establish if there could be significant differences at the optimum point.

6.7 Conclusion

In this study, it was discovered that *Irvingia* adhesives had good water absorption and thickness swelling properties. The water absorption and thickness swelling of most panels made with *Irvingia*-based adhesives met the minimum requirements as stated in ANSI A208.1 standard except IGC and IWC panels. The mechanical properties of the panels also met the minimum requirements as stated in the ANSI A208.1 except for IGC and IWC. According to the ANSI A208.1 standard all panels used in this experiment, with exception of IGC and IWC, are within the category grade of 1-L-1. These panels are recommended to be used as core material for solid doors. Finally, *Irvingia*-based panels have great potential to be used in the wood panel industry.

Chapter 7

Conclusions and suggestions for future studies

7.1 Introduction

This study opens a new area of insight into research based on the development of natural wood adhesives from the extract of *Irvingia* species seed kernels. The intention was to reduce the hazardous effect on both humans and the environment of formaldehyde emissions from composite products bonded with formaldehyde-based adhesives. The technology of the *Irvingia*-based adhesives has been evaluated in pharmaceutical application (Eraga et al. 2014; Ikechukwu and Salome 2013) but to the best of our knowledge, this is the first time that these adhesives have been investigated in the sphere of wood composite development. The following sections discuss the conclusions from this study and suggest recommendations for future study.

7.2 Conclusions

This study evaluated properties and potential use of *Irvingia gabonensis* and *Irvingia wombolu* kernel extracts as an eco-friendly wood adhesive in the wood composites industry.

Based on the objectives of this study, the following conclusions can be drawn:

- The first phase of the study investigated the properties of extracts from the seed kernels of two *Irvingia* species – *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW) – as natural wood adhesives. Three extraction methods, based on various solvent/solute media, were compared in terms of yield and extracts properties. These were:
  - Sodium chloride extraction method
  - Sodium Metabisulphite extraction method
  - Water extraction method

  The yield from different extraction methods for the two species was determined by weighing the dried *Irvingia* extract and calculated on wet basis. The pH of all the *Irvingia* extracts was measured with a digital pH meter (Mettler Toledo S220). The thermal stability of the *Irvingia* extract powdered samples was analysed using a TGA Q50 thermogravimetric apparatus. The adhesion properties of the extracts was tested using a standard method based on the use of glass fibre paper strips.
  The post hoc test analysis showed that there was no significant difference ($p > 0.05$) in the effect of species and extraction methods on the adhesive yield, except for sample IWM which was significantly different from other samples. The pH results show that

Irvingia extracts are mildly acidic. The TGA results revealed that extraction methods have a major effect on the decomposition behaviour of all samples irrespective of species variations. Based on the strength comparison with commercially available urea resin Bondtite®, extract produced using water extraction exhibited comparable properties. The results of the study indicate that *Irvingia* kernel extract is a promising source for non-formaldehyde-based adhesives in wood composite production.

- The second phase evaluated the effect of modification on the properties of the binder produced from the seed kernels of two *Irvingia* wood species i.e. *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW), using a few selected modifying agents including glutaraldehyde, glyoxal, epichlorohydrin and an acid/base type process modification.
  The modified and unmodified *Irvingia* adhesive samples were analysed with FTIR spectroscopy operated in Attenuated Total Reflectance (ATR) mode. The thermal stability analyses of the adhesives powdered samples were analysed using a TGA Q50 TGA apparatus. The adhesive shear strength of the modified extracts was tested on wood veneers according to the American Society for Testing and Materials standard (ASTM D – 906-64).
  The appearance of new characteristic absorption bands in modified adhesives as evidenced in FTIR results, which are absent in unmodified adhesives confirmed modification of the adhesives which occurred due to interaction between methoxyl functional groups in hexamine and hydroxyl groups in wood, hardeners and starch molecules. TGA and DTG results showed that modified adhesives have low thermal degradation and good thermal stability. The highest values of adhesive shear strength of the modified samples were about 16% higher than panels bonded with IGN (unmodified) adhesives. The results indicated that modification of *Irvingia*-based adhesives made a great contribution to their performance as natural wood adhesives.

- The third phase of the study investigated the physical and mechanical properties of experimental panels made with pine *(Pinus elliottii)* wood particles, using modified *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW) extracts as a binder. FTIR analysis was performed to study any variation between the FT-IR spectra of the manufactured panels produced using different adhesives. The properties of the formed panels were evaluated to investigate the effect of modification on the flexural strength and dimensional stability of the panels. Flexural test specimens were tested according to ASTM D1037-06a standard using an Instron testing machine fitted with a 5 KN load cell, operated at a rate of 5 mm/min. The specimens were tested to failure and the MOR and MOE were calculated from the formula outlined in ASTM (2006).

FT-IR results could not effectively detect variations in the chemical structures related to the different modifications and this may be due to low contents of modifiers. It was observed from the physical properties evaluated, pending ageing studies, that panels produced with modified *Irvingia* adhesives are promising for outdoor applications because they exhibited good water-resistance properties. The flexural results showed that all the panels manufactured with *Irvingia*-based adhesives and Bondtite® met the minimum requirements and can be categorised within grade 1-L-1 according to ANSI A208.1 standard, except panels bonded with IWC and IGC adhesives. These panels are recommended to be used as core material for solid doors. The results from the study show that *Irvingia* kernel adhesives may be considered as a potential environmentally friendly adhesive for wood composite manufacture.

7.3 Suggestions for future studies

- **Materials from other sources**

  A study of the properties of extract from other fruits seed kernel should be encouraged and comparison of these extracts would be helpful in their optimal utilisation for appropriate bonding requirements as well as shedding light on their adhesion mechanism.

- **Durability of wood products bonded with *Irvingia*-based adhesives**

  Accelerated ageing and natural ageing tests should be undertaken to access the ageing resistance properties of wood composites bonded with *Irvingia*-based adhesives. The fungicidal and termiticidal effects on the mechanical properties of wood to wood bonding with *Irvingia*-based adhesives should be investigated. Research should be encouraged to provide the durability-or-ageing-relevant parameters of *Irvingia*-based adhesives to promote its industrial application.

- **Commercialisation of *Irvingia*-based adhesives**

  Prior to the industrial usage of *Irvingia* kernels extract as industrial feedstocks for wood adhesive applications, there is a need to investigate growth variations such as growing season and the location of *Irvingia* trees on the quality of *Irvingia*-based wood adhesives. There should be collaboration between wood adhesive manufacturers and wood composite manufacturers to address the variation in raw material qualities, cost and quantity and to satisfy the needs of the end users, with a sustainable manufacturing

approach. Additionally, more effort should be put into developing new processes, products and conscientise markets that will adopt the features of bio-based wood adhesives, using statistical process control.

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Appendix 1

Declaration by candidate and co-authors

1. With regard to Chapter 2 (Paper I – Production and Evaluation of Formaldehyde-Free Wood Adhesives from Renewable Resources), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Conceptualised and wrote the paper	80

The following co-authors contributed to the chapter:

Name	E-Mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmein@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Contributed to the writing of the paper, read and approved them	10

2. With regard to Chapter 4 (Paper II – Properties and characteristics of novel formaldehyde free wood adhesives prepared from *Irvingia gabonensis* and *Irvingia wombolu* seed kernel extracts), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Conceptualised and wrote the paper	70

The following co-authors contributed to the chapter:

Name	E-mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmein@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
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Stephen Amiandamhen	amiandamhen@sun.ac.za	Contributed to the writing of the paper, read and approved them	10

3. With regard to Chapter 5 (paper III – Evaluation of *Irvingia* Kernels extract as biobased wood adhesive), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Conceptualised and wrote the paper	80

The following co-authors contributed to the Chapter:

Name	E-Mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmein@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Contributed to the writing of the paper, read and approved them	10

4. With regard to Chapter 6 (paper IV – Performance evaluation of a natural based adhesive derived from *Irvingia* wood species kernel extracts on wood panel production), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Conceptualised and wrote the paper	80

The following co-authors contributed to the chapter:

Name	E-Mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmein@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Contributed to the writing of the paper, read and approved them	10

5. With regard to Chapter 7 (paper I – Techno-economic analysis for small scale production of *Irvingia*-based adhesive in South Africa), the nature and scope of my contribution were as follows:

Nature of contribution	Extent of my contribution
Conceptualised and wrote the paper	80

The following co-authors contributed to the chapter:

Name	E-Mail address	Nature of contribution	Extent of contribution (%)
Martina Meincken	mmein@sun.ac.za	Contributed to the writing of the paper, read and approved them	10
Luvuyo Tyhoda	ltyhoda@sun.ac.za	Contributed to the writing of the paper, read and approved them	10

Appendix 2:

Techno-economic analysis for small scale production of *Irvingia*-based adhesive in South Africa

1 Introduction

The global market for renewable products was estimated to be USD49.0 billion in 2015 by a global market research company MarketsandMarkets, with projection to reach USD84.3 billion by 2020 at a compound annual growth rate of 11.47 percentage (Zhonggi 2017). The rate at which this development progresses may be enhanced through the adoption of an implementation of such manufacturing concepts as the biorefinery concept with the intention to maximise profit and benefit for sustainability development (Abduh, Manurung, and Heeres 2017).

There are various mechanisms involved in a biorefinery for the production of biobased products from various biomass feedstock (Abduh, Manurung, and Heeres 2017). *Irvingia* kernels are of particular interest as there is renewed interest in the domestication of *Irvingia* species globally due to the potential use of its kernels as raw materials for a wide range of applications such as biodiesel production, cosmetics, perfumes, soap and weight-loss supplements (Ainge and Brown 1998; Singh 2007). From the viewpoint of a biorefinery, the identification of high added-value outlets for *Irvingia* kernels is highly relevant as it increases the profit for the *Irvingia* tree plantation.

The *Irvingia* seeds consist of a kernel with weight ranges from 0.41–7.58 g embedded in a shell with weight ranges from 4.9–30.9 g. The kernel contains 68–75% of crude fat surrounded in a carbohydrate/protein-rich matrix which can be extracted by simple low-cost extraction methods for adhesives application (Singh 2007). *Irvingia* kernel extracts are a valuable source for the production of renewable wood adhesives with desirable bonding properties. These extracts are byproducts obtained after the kernel fat content has been used for the manufacture of various products such as cosmetics, biofuel, cooking oil, season cubes, soaps and confectionaries (Bello, Anjorin, and Mogaji 2011; Ekpe et al. 2015).

The production of *Irvingia* adhesives can be carried out on different scales. For large industrial scales (100 kton/y up to 250 kton/y), the processing equipment components have greater efficiencies albeit at expensive capitalisation and on-site construction. The *Irvingia* kernels can be obtained in abundance from *Irvingia* tree plantations. However, the transport of raw material

from its source and also the products to the end user are normally over long distances entailing high transport costs.

Irvingia wood adhesives can also be produced in small-scale systems (<15 kton/y) which require less complicated and less expensive processing technologies and can be applied in rural areas. This may lower the capital cost and reduce the transportation cost of both the feedstock and product as well as improving the overall efficiency of the market delivery. This chapter reported a preliminary techno-economic evaluation for small-scale production of *Irvingia* wood-based adhesives in South Africa using different modification methods. The production cost for *Irvingia* wood-based adhesives was estimated and a sensitivity analysis was performed to evaluate the potential application of *Irvingia* wood-based adhesives.

2 Process description and mass balances

The extract origins and modification methods used to prepare *Irvingia* adhesive samples are indicated by notations in Table 1 and these notations are their brand names. The market price of various wood adhesives available in South Africa is presented in Table 2 for comparison with the estimated production price of *Irvingia*-based adhesives.

Table 1: Extract origins, modification methods and abbreviations of the *Irvingia* adhesive

Extract origins	Modification methods	Notation
Irvingia	Epichlorohydrin modified	IEM
Irvingia	Glutaraldehyde modified	IGM
Irvingia	Glyoxal modified	IGLM

Table 2: Extract origins, modification methods and abbreviations of the *Irvingia* adhesives

Wood Adhesives	Quantity	Price	Price/litre	References - Date cited: 02/11/2018
Rolfes Multipurpose Wood Glue	5 Litre	R 320	R 64	https://www.takealot.com https://bit.ly/2CXgles
Adhesive Wood Glue ALCOLIN	1LT	R 111.27	R 111.27	https://www.farmcity.co.za https://bit.ly/2QcMR5v
Everbuild Wood Adhesive Bottle 502	500ML	R 86 (On promotion)	R 172	MASSBUILD (PTY) LTD [25] https://bit.ly/2P3RJh5
Alcolin Adhesive Professional Wood Glue	250ML	R 85.82	R 343.28	https://www.stockclearanceportal.co.za https://bit.ly/2Jx8D1n
ALCOLIN Ultra Wood Glue	500ML	R 119.90	R 239.80	https://www.toolcraft.co.za https://bit.ly/2OlBgPR
Alcolin Cold Glue Wood Glue	125ML	R 32	R 128	https://www.takealot.com https://bit.ly/2CXK7W3
Bostik Art And Craft Glue - White	100ML	R 50	R 1000	MASSBUILD (PTY) LTD [25] https://bit.ly/2ETtL3c
WOOD GLUE GLUEDEVIL	1LT	R 90	R 90	https://diyshop.co.za https://bit.ly/2DibHhD
Glue Wood Water Resistant Ponal Henkel	500ML	R 79.26	R 158.52	https://www.farmcity.co.za https://bit.ly/2qoBLPF
Fortseal Wood Glue	500ML	R 49.00	R 98	https://www.makro.co.za https://bit.ly/2Dj3J8a
Genkem Wood Glue Quickset	1LT	R 98	R 98	MASSBUILD (PTY) LTD [25] https://bit.ly/2qpgWDG
ALCOLIN Glue Wood Cold	2.5LT	R 459	R 183.6	https://www.takealot.com https://bit.ly/2Qe44vy
ALCOLIN Glue Wood Cold	5LT	R 559	R 111.8	https://www.takealot.com https://bit.ly/2OnBRka
PRITT PONAL WOOD GLUE	100ML	R 28.00	R 2800	https://www.cliqtosave.com https://bit.ly/2Qi0d0D
Ponal Wood Glue	5LT	R 445	R 89	MASSBUILD (PTY) LTD [25] https://bit.ly/2PKlxhb
Average price			**R 379.15**	

2.1 Process description for extract production

The production scale was set at an input of 98.7 kg wet *Irvingia* kernel per day, which is the maximum capacity of the medium size-dispersing tank. The kernels typically have a moisture content of around 10 wt%. Directly after harvesting, the kernels are dried in an oven operated at 40 °C to reduce the moisture content to 7 wt% to improve storage stability, thereby making 95.7 kg available for production per day. With an estimated yield of 30 wt% of Irvingia extract on dry

kernels, the estimated *Irvingia* extract is 28.7 kg/day with an assumption of working with dehulled kernels and no loss during kernel milling. When assuming 24 h per day of extraction process for 306 days a year, the annual *Irvingia* extract production of the unit is 30 ton. An overview of the extract and *Irvingia* adhesives production units is shown in Figures 2 and 3. The seeds are then stored in a sealed bags as shown in Figure 1; these are properly stored in a closed container.

Figure 1: Packed dried African mango seed kernel

The kernels are dehulled to remove the coat and thereafter milled using a hammer mill fitted with a 1 mm sieving slice. To produce 28.7 kg of classified extract per day, 97.7 kg of powdered cotyledon is dispersed in 1 914 litres of water in a mixing tank. The mixture is gently stirred for 1 h with the aid of a magnetic stirrer. The dispersion was homogenised for about 1 h and left for 24 h. The mucilage formed was then filtered through a separator to obtain a viscous filtrate (gum). The filtrate was centrifuged (Allegra 6R centrifuge, Beckman Coulter™, USA) at 3 440 rpm for 10 min to separate the fat. The gum was then vacuum-dried for further use.

2.2 Mass balances for extract production process

The mass balance of the extract production process is shown in Figure 2. It assumes an input of 100.7 kg/d of wet *Irvingia* kernels (10 wt% water). After drying, 97.7 kg/d of dried kernels (7 wt% water) are milled. Assuming no loss during kernel milling 97.7 kg/d of powdered cotyledon were dispersed in 1 954 kg/d of water. Assuming a crude yield of 31 wt% on wet seeds, it is estimated that 30.3 kg/d crude extract and 67.4 kg/d of extracted fat can be obtained. After centrifuging of the crude extract, an estimated 2 kg/d of sediment is formed whereas 28.3 kg/d of classified *Irvingia* extract is vacuum dried and stored for further use.

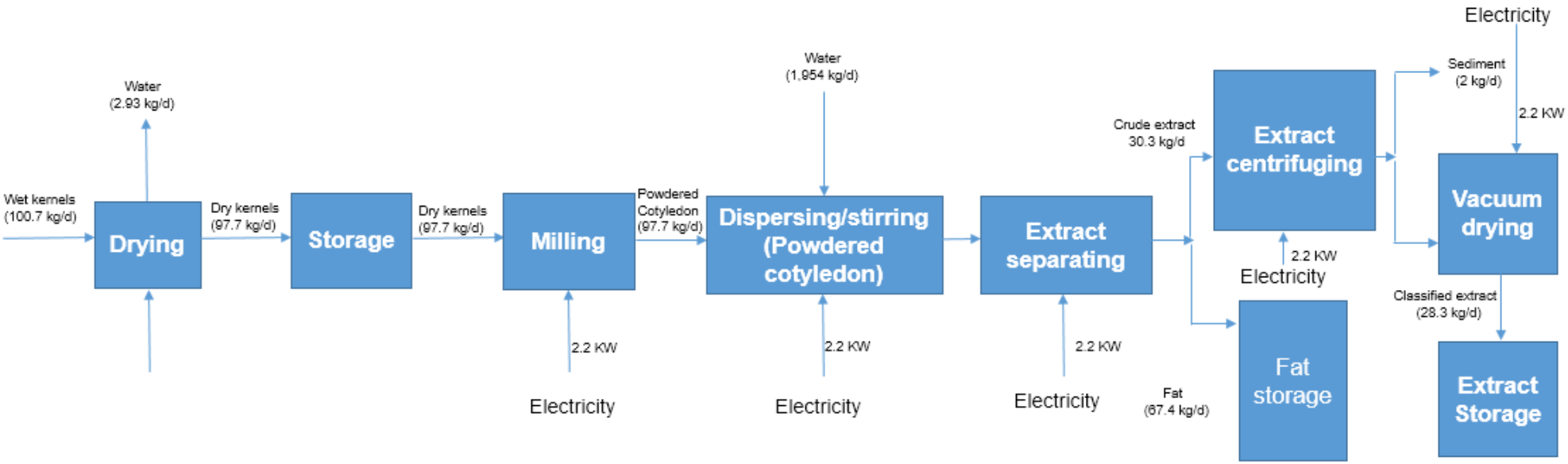

Figure 2: Process flow diagram and mass balance for the production of *Irvingia* extract

3 Process description and mass balance for the adhesives

3.1 Adhesive production process description

The production of *Irvingia* extract in the extraction unit is approximately 28.3 kg/d, with reference to the previous section for details. When assuming for 30 tonne/year adhesive production for each brand, the estimated production scale of the extract unit is approximately 28.3 kg/d (24 h extraction operation per day for 306 days per year). An overview of the *Irvingia* adhesive production process is shown in Figure 3. It involves storage vessels for feeds and products, a boiler incorporated with stirrer, and a cooling tower.

3.2 Mass balances for adhesive production process

The mass balance of the process is provided in Figure 3 and is based on a 28.8 kg/d *Irvingia* extract input. The production was carried out using different hardeners. The hardeners are epichlorohydrin, glutaraldehyde and glyoxal with hexamine as a crosslinker. To produce 98 kg/d of adhesives which is equivalent to 30 tonne/year of adhesive, based on 306 days operation per year, 28.8 kg/d of dried powder extract was dissolved in 53.89 kg/d of water using a big boiler incorporated with a stirrer. The temperature was set at 60 ˚C and the mixture was stirred gently for about 1 h. The solution was cooled to a temperature of 25 ˚C in a cooling tower. 9.4 kg/d of hardener and 5.9 kg/d of hexamine were added separately to the extract to produce the binder. Volumes were adjusted for loss of water. The mixture was continuously stirred for 10 min and then left to cool to room temperature.

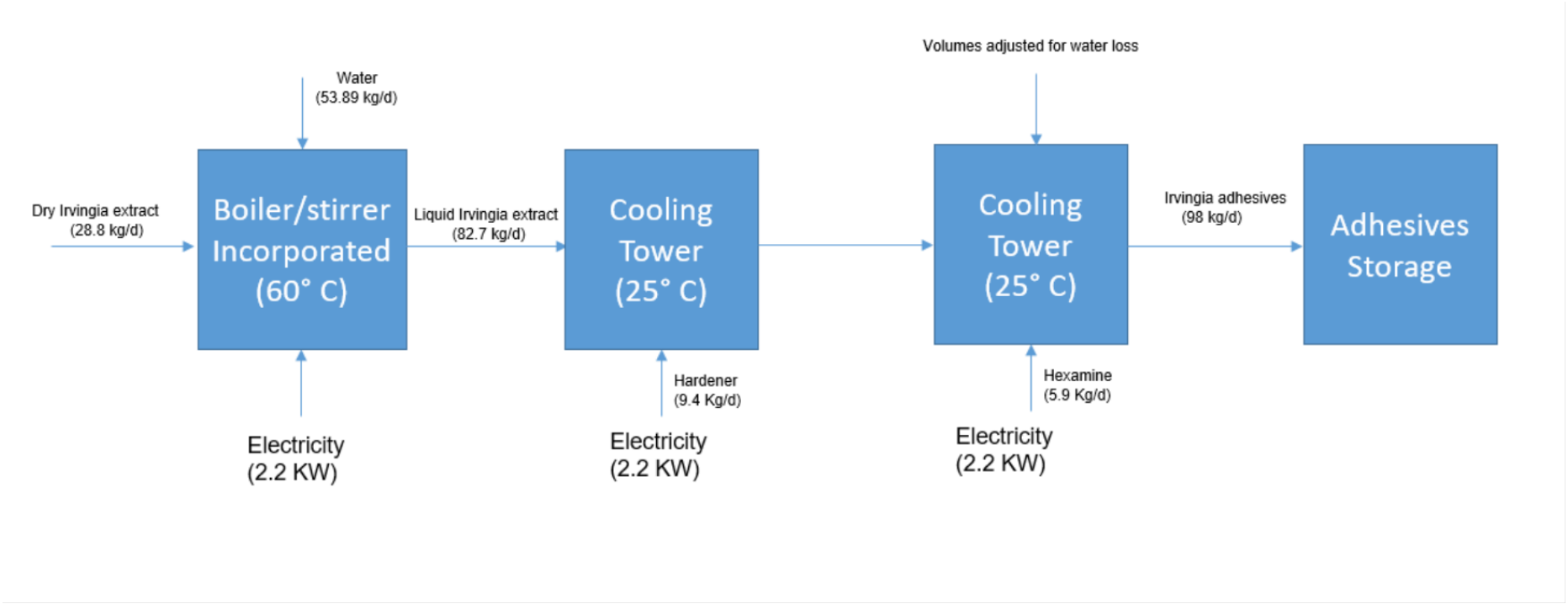

Figure 3: Process flow diagram and mass balance for the production of Irvingia-based adhesives

4 Cost estimation and sensitivity analysis

The total capital and production cost estimates for production of *Irvingia* adhesives are based on a cost estimation procedure by (Abduh, Manurung, and Heeres 2017b). Overheads, research, financing as well as distribution and marketing costs are excluded from the calculation of the total production costs, as the small-scale unit is expected to require a limited amount of space.

4.1 Cost estimation

The total equipment cost based on the process description and mass balance as shown in Figures 2 and 3 are estimated at R263,043 (Table 3). This cost includes storage facilities for the kernel silo tank as well as process equipment such as spray dryer, centrifuge and hammer mill. The costs are based on online prices.

Table 3: Estimated total equipment cost for a 30-Ton/Y *Irvingia* adhesives processing unit

Item	Cost (R)
Storage facilities	
Kernel storage (silo tank 5000L)	4,000
Extract storage tank (10 000L)	5,000
Hexamine storage tank (2,500 L)	2,500
Glyoxal storage tank (2,500 L)	2,500
Epichlorohydrin tank (2,500 L)	2,500
Glutaraldehyde storage tank (2,500 L)	2,500
Adhesive storage tank (10 000L)	5,000
Subtotal storage facilities	**24,000**
Process equipment	
Hammer mill, 2.2kw single phase high speed motor (2850 rpm)	10,000
Kernel drying (Hot Air Circulation Drying Oven)	50,000
Weighing balance, 500 kg	1,543
Separator	18,000
Soaking/ mixing tank, boiler incorporated	20,000
Centrifuge	50,000
Spray dryer	35,000
Cooling tower (40Ton FRP Cooling Tower)	40,000
Auxiliary Equipment	
(Compressor, pipes, fillings, etc.)	14,500
Subtotal process equipment	**234,043**
Total equipment cost	**263,043**

The total capital investment (TCI) for the small-scale *Irvingia* adhesives production facility was estimated to be R422,609.53. This value is the sum of the fixed capital investment (FCI) and working capital investment (WCI), which were evaluated independently (Table 4). Total raw material cost for each brand is presented in Table 5. An overview of the total production cost for a 30-ton/y Irvingia adhesives processing unit in South Africa is given in Table 6.

The cost of the *Irvingia* seed kernel extract was estimated at #3,375/kg. Assuming a currency exchange of #25/R, this equals to R40.5/kg. The annual electricity required for the process was

estimated to be around 8800 KWh. Assuming an electricity cost of R2.1032/KWh, the annual cost for electricity is R18,508.16. The quantity of water required to produce 30 ton of adhesives annually was estimated to be around 8.8 ton. Assuming industrial water cost of R 29.93/litres, the annual cost for water is R493,845.00. The wages for the employees are based on the standard salary for employment in South Africa (R51.28/h). Assuming 4 employees working a 6 h shift per day and that the unit is in operation 24 h/d, the total employee cost is R376,600.32.

Table 4: Estimated total capital cost for a 30-ton/y *Irvingia* adhesives processing unit

Item	Cost (R)
Direct Cost (DC)	
Equipment cost (E)	263,043.00
Instrumentation and Control (0.4E)	105,217.20
Electrical Distribution System (0.1E)	26,304.30
Establishment of Equipment (0.45E)	118,369.35
Total DC	249,890.85
Indirect Cost (IC)	
Technical and Supervision (0.15DC)	37,483.63
Unexpected Expenses (0.15FCI)	50,713.14
Total IC	88,196.77
Fixed Capital Investment (FCI)	
FCI = DC + IC	338,087.62
Working Capital Investment (WCI)	
WCI = 0.2TCI	84,521.91
Total Capital Investment (TCI)	
TCI = FCI + WCI	422,609.53

Table 5: Raw material costs for a 30-ton/y modified *Irvingia* adhesives processing unit

Raw materials	Annual use (ton)	Cost (R)
IEM		
Irvingia seed kernel extract	8.8	4,077,297.00
Hexamethoxymethylmelamine (Hexamine)	1.8	1,836,000.00
Process water	16.5	493,845.00
Epichlorohydrin ≥ 99%	2.9	2,300,280.00
Total material cost		**8,707,422.00**
IGM		
Irvingia seed kernel extract	8.8	4,077,297.00
Hexamethoxymethylmelamine (Hexamine)	1.8	1,836,000.00
Process water	16.5	493,845.00
Glutaraldehyde solution (Grade II, 25% in H_2O)	2.9	6,786,000.00
Total material cost		**13,193,142.00**
IGLM		
Irvingia seed kernel extract	8.8	4,077,297.00
Hexamethoxymethylmelamine (Hexamine)	1.8	1,836,000.00
Process water	16.5	493,845.00
Glyoxal solution (40 wt. % in H_2O)	2.9	1,954,600.00
Total material cost		**8,361,742.00**

Table 6: Estimated total production cost for a 30-ton/y *Irvingia* adhesives processing unit

Item	Cost (R)			
Raw materials/year		IEM	IGM	IGLM
		8,707,422	13,193,142	8,361,742
Employees' salaries/year	376,600.32			
Electricity cost/year	18,508.16			
Maintenance (0.01 FCI)	6,939.69			
Operating supplies (0.1 salary)	37,660.03			
Supervision (0.1 salary)	37,660.03			
Administration cost (0.02 salary + Maintenance + supervision)	8,424.00			
Depreciation (0.1 FCI)	69,396.93			
Subtotal production		9,262,611	13,748,331	8,916,931
Co-product credit-extracted fat	4,204,000.00			
Total production cost (TPC)		5,058,611	9,544,331	4,712,931

Taking into account the total *Irvingia* adhesives production of 30 ton/y for each sample, the Irvingia adhesives production cost for each sample is R168.62/kg, R318.14/kg and R153.44/kg for IGLM, IGM and IEM respectively. These values will be R151.76/L, R289.51/L and 142.96/L respectively, when assuming an *Irvingia* adhesives density of 0.91 kg/L. For comparison, the average market price of wood adhesives in South Africa as shown in Table 16 is approximately R 379.15/kg. As such, the *Irvingia* adhesives may be a competitive product for wood composite production.

4.2 Sensitivity analysis

Sensitivity analyses were performed to investigate the effect of input variables on the production costs of three brands of *Irvingia*-based wood adhesives. These variables include: employees' salaries, cost of *Irvingia* kernels, total raw materials cost, co-product extracted fat and electricity. The sensitivity bounds for the input variables were set at 50 and 150% of the base case. For all units (IEM, IGM and IGLM), the employees' salaries have limited effect on their production costs. Likewise, the cost of the electricity used in the course of their production has the least effect on the production cost and as such is of less importance.

The results of sensitivity analysis for IEM brand are shown in Figure 4. Total raw materials cost has the largest effect on the production cost. A reduction in the total cost of the raw materials to 50% leads to a decrease in the IEM price to R21/L. A rise in the total raw materials cost to 150% leads to an increase in the IEM price to R286/L. Other important input variables are the price of co-product extracted fat and the cost of the *Irvingia* kernels.

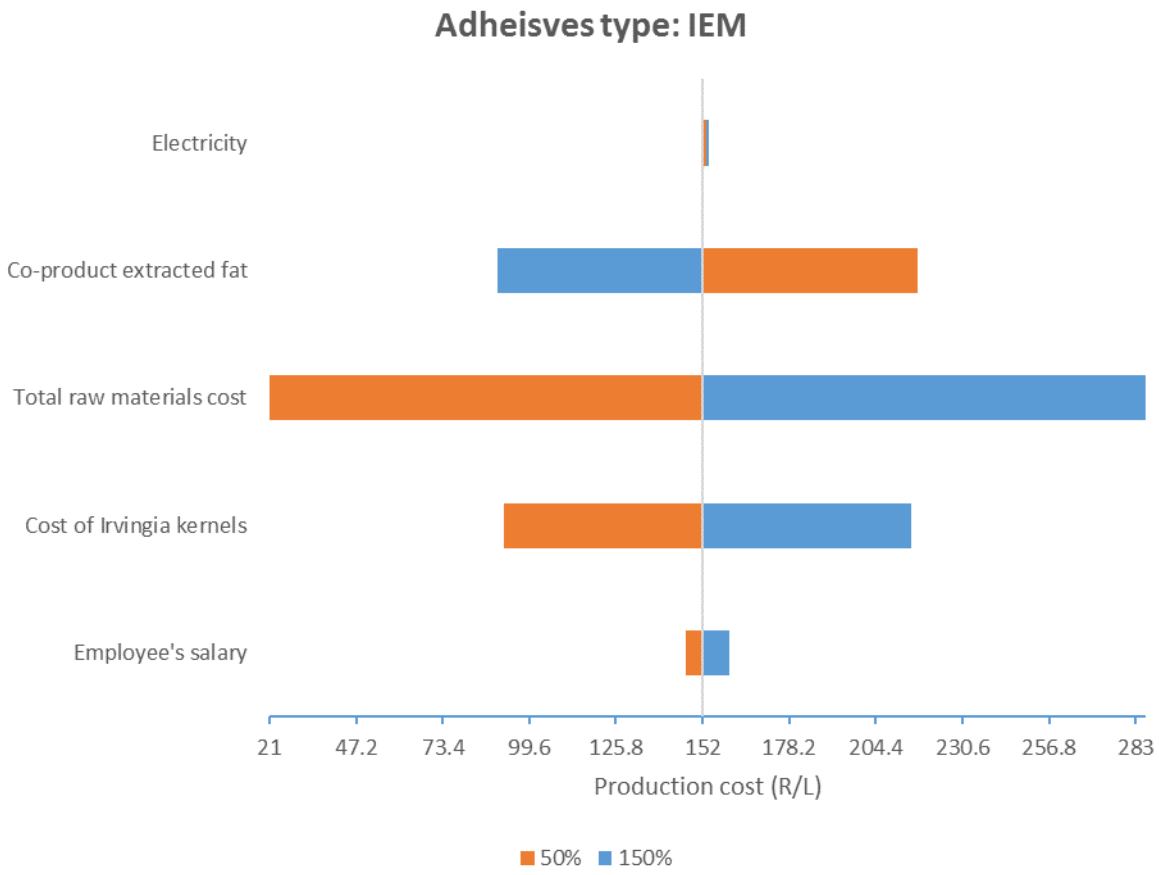

Figure 4: Sensitivity analysis for IEM bio adhesives processing unit in Stellenbosch, South Africa

The results of sensitivity analysis for IGM brand are shown in Figure 5. The most influencing economic parameter is the cost associated with the total raw materials. Change in the cost of total raw materials has a substantial effect on the production cost. By achieving a 50% decrease in the cost of total raw materials, the production cost reduced to R89/L. A 50% rise in the total raw materials cost leads to an increase in the IGM price to R490/L. Contrarily for a 50% increment in the price of co-product extracted fat, the production cost reduces to R 226/L.

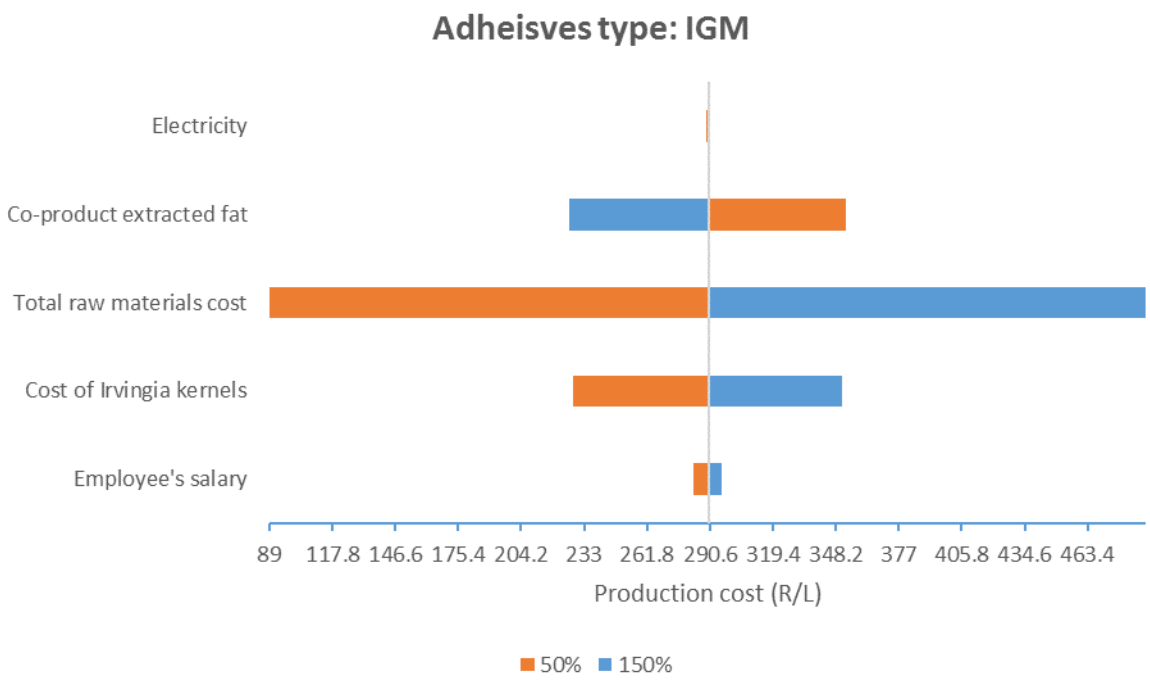

Figure 5: Sensitivity analysis for IGM bio adhesives processing unit in Stellenbosch, South Africa

The results of sensitivity analysis for IGLM brand are presented in Figure 6 and the trend is similar to that of IEM and IGM. Total raw materials cost has the major effect on the production cost. A drop in the total cost of the raw materials to 50% leads to a decrease in the IGLM price to R16/L. A rise in the total raw materials cost to 150% leads to an upsurge in the IGLM price to R270/L. Other important input variables as explained above are the price of co-product extracted fat and the cost of the *Irvingia* kernels.

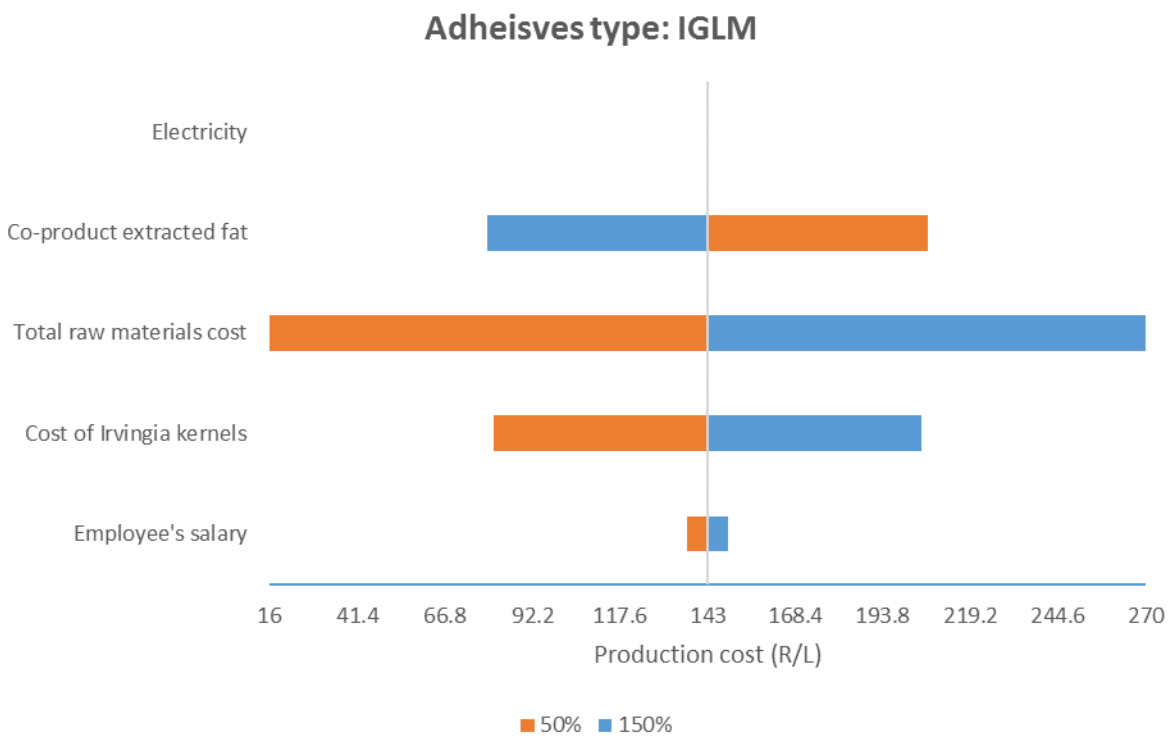

Figure 6: Sensitivity analysis for IGLM bio adhesives processing unit in Stellenbosch, South Africa

5 Conclusion and outlook

The production cost for *Irvingia*-based adhesives (IEM, IGM and IGLM) in a small-scale production unit (30 ton/y) in South Africa were estimated to be R168.62/kg, R318.14/kg and R153.44/kg for IGLM, IGM and IEM respectively. The employees' salaries as well as the cost of the electricity used in the production of the three brands have the least effect on their production cost and they should not be considered for review. The major variable is the total raw materials cost in the unit. When the cost increases by 50%, the production costs of the three brands escalate to R318/kg, R544/kg and R300/kg for IEM, IGM and IGLM respectively. The effect of the other two input variables (cost of *Irvingia* kernels and co-product extracted fat) is significant and all show about equal sensitivity for each brand. For comparison, the average market price of wood adhesives in South Africa as shown in Table 2 is approximately R379.15/kg whereas the average price of *Irvingia*-based adhesives is 213.4/kg. As such, the *Irvingia*-based adhesives may be a competitive product for the production of wood composites in South Africa.